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DIE SAMESTELLING VAN DIE OLIE VAN *SCLEROCARYA CAFFRA* SOND. (MAROELA) PITTE

deur

S. P. LIGTHELM, H. M. SCHWARTZ en M. M. VON HOLDT

SUMMARY

The oil content of *Sclerocarya caffra* Sond. or Maroola kernels has been determined, the kernels constituted 13.9 per cent of the seeds and contained 53.5 per cent of oil. The oil had the following constants: S.G. (25° C.), 0.9051; n_{D}^{20} , 1.4630; Acid Val. 14.8; I.V. (Wijs), 74.4; Sap. Val., 190.0; Acetyl Val., 8.4; Reichert-Meissel Value, 0.35; Polenske Val., 0.39; per cent unsap. matter, 2.4. The following composition was calculated for the fatty acids (calculated as percentage by weight): palmitic 16.1, stearic 5.0, C_{20} -sat. 0.1, C_{22} -sat. 1.0, hexadecenoic 1.0, oleic 66.7, linoleic 7.3, linolenic trace, C_{20} -2H 2.7. This composition is typical of that of oils of other species in the family Anacardiaceae.

OPSOMMING

Die olie inhoud van Maroela-pitte (*Sclerocarya caffra* Sond.) is bepaal; die kerne maak 13.9 persent van die pit uit en bevat 53.5 persent olie. Die olie het die volgende konstantes gehad: S.G. (25° C.), 0.9051; n_{D}^{20} , 1.4630; suurgehalte, 14.8; J.G. (Wijs), 74.4; Vers. Get., 190.0; Asct. Waarde, 8.4; Reichert-Meissel Get., 0.35; Polenske Get., 0.39; persent Onvers. Mat., 2.4. Die volgende samestelling (berekend as gewigspersentasie) is vir die vetsure bereken: palmitien 16.1; stearien, 5.0; C_{20} -vers. 0.1; C_{22} -vers. 1.0; heksadekeen, 1.0; olien, 66.7; linolien, 7.3; linoleen, spoor, C_{20} -2H, 2.7. Hierdie samestelling is soortgelyk aan die van ander olies van die Anacardiaceae-familie.

Sclerocarya caffra Sond. (Maroela-Phill. gen. bl. 381)—'n sub-familie van die Anacardiaceae-familie, is 'n binnelandse spesie van die tropiese dele van Afrika en Madagaskar¹. Daar bestaan drie of meer spesies en daar is berig dat almal eetbare vrugte dra. Die Maroela word volop aangetref in die laeveld (bosveld) van Transvaal, in die warmer dele van Natal en Soeloeland, in Mosambiek, in Swasieland, in die twee Rhodesiës, en ook in Madagaskar. In Madagaskar staan dit bekend as die Sakoaneutboom². Die boom groei betreklik vinnig en as dit volgroeid is lewer dit jaarliks groot dragte vrugte. Die vrug, 'n steenvrug, val van die boom voordat dit heeltemal ryp is, die groen skil verander langsaam na geel met 'n hele aantal kenmerkende roesagtige kolletjies. Die vrug het 'n baie aangename, deurdringende geur, 'n effense sitroensuurmaak en word as een van die populêrste wilde vrugte beskou. Van die sap van die vrugte kan 'n alkoholiese drank (Witblits) gestook word en dit kan selfs gebruik word om 'n jellie van te maak³.

Die Maroela kern bestaan uit drie afsonderlike dele en is omring deur 'n harde veselagtige dop wat moeilik gebreek kan word. Ons het gevind dat die dop die maklikste in 'n skroef gebreek kan word, waarna die kerne verwyder kan word, of die olie uit die totale pit geëkstraheer kan word.

Die pitte en kerne van die Maroela was voorheen deur Jones⁴ ondersoek wat die volgende vetsuursamestelling vir die olie bereken het: stearien en palmitiensure 9 persent, olien- en linolien sure 91 persent; die Imperial Institute⁵ het die olie-inhoud van die pitte bepaal, terwyl die pitte van die Madagaskar-spesies deur Jumelle⁶ ondersoek is. In 1921 het Rindl⁶ Maroelapitte bespreek as 'n moontlike bron van 'n nie-droënde olie in Suid Afrika, maar hy het tot die gevolgtrekking gekom dat die grootskaalse ekstraksie van die olie beperk word deur die hardheid van die pit.

Ekstraksie en Ondersoek van die Olie

Die pitte wat vir die ondersoek gebruik is, is in April 1949 in die Middelburg-Groblersdal distrikte bymekaar gemaak. In sommige gevalle was die pitte met gedroogde vrugte en skille bedek, wat eers verwyder is voordat die samestelling van die pitte bepaal is. Die pitte is eers geweeg, dan in 'n skroef gebreek en die kerne verwyder en weer geweeg. Die kerne van pitte (50 pond) is verwyder en in 'n vleismeul gemaal. Geweegde hoeveelhede is in 'n Soxhletapparaat geplaas en afsonderlik met asetoon en petroleum eter (40° – 60° C.) geëkstraheer. Nadat die ekstraksies 10 tot 12 uur geduur het, is die oplosmiddels met vars oplosmiddels vervang en die ekstraksies vir nog 10 tot 12 uur herhaal. Die totale oplosmiddel (van elke afsonderlike ekstraksie) is daarna deur 'n geweegde distilleerfles afgedistilleer en die olie wat agtergebly het onder verminderde druk op 'n stoombad drooggemaak. Die olie het 'n effense bruin kleur met 'n neutagtige smaak gehad en is met aktiewe koolstof in asetoon ontkleur. Die gesuiwerde olie het 'n ligter kleur gehad en is feitlik smaakloos. Die grootskaalse ekstraksie van die olie is in 'n groot koper ekstraktor uitgevoer, die geïsoleerde olie is gedroog en met aktiewe koolstof ontkleur, waarna dit in 'n donker fles onder koolstofdioksied gebêre is.

Die olie inhoud van die kerne, sowel as die konstantes van die gesuiwerde olie word in Tabel I aangegee:

TABEL I

(a) Analise van Maroelapitte

| | Ons bevindings | Voorheen gerapporteer ^a |
|---------------------------------|-------------------|---------------------------------------|
| Gemiddelde gewig van pitte (g.) | 5.93 | 4.0 |
| Gemiddelde gewig van kerne (g.) | 0.82 | — |
| Kern as persentasie van pit | 13.9 | 12.0 |
| Olie inhoud van kern (persent) | 53.8 | — |
| Olie inhoud van pit (persent) | 7.5 | 5-6.3 |
| Voggehalte van kern (persent) | 4.97 | 5.0 |

(b) Konstantes van gesuiwerde Maroela olie

| | Ons bevindings | Voorheen gerapporteer ^a |
|--|-------------------|---------------------------------------|
| Soortelike gewig ($25^{\circ}/25^{\circ}$) | 0.9051 | 0.9167 |
| Brekingsindeks (25°) | 1.4630 | 1.460 (40°) |
| Suurgehalte | 14.8 | 3.7 |
| Joodgetal (Wijs-een uur) | 74.4 | 76.6 |
| Versepingsgetal | 190.0 | 193.5 |
| Asetielwaarde | 8.4 | — |
| Reichert Meisselgetal | 0.35 | 0.1 |
| Polenskegetal | 0.39 | 0.45 |
| Onverseepbare materiaal (persent) | 2.4 | 0.6 |

Die absorpsiespektrum van die ru en gesuiwerde olie is tussen die golflengtes 220–330 μ ondersoek, en toon aan dat beide olies net spore van toegevoegde onversadigde sure bevat.

Die onverseepbare fraksie van die olie wat geïsoleer is volgens die S.P.A.-metode⁷ bevat 'n aansienlike hoeveelheid koolwaterstowwe (8.4 persent) en 'n klein hoeveelheid (0.9 persent) α-gliseriel eters. Die sterolinhoud van die fraksie is 37.5 persent, terwyl die orige 53.2 persent nie geïdentifiseer kon word nie. Omdat klein hoeveelhede materiaal (onverseepbare fraksie) beskikbaar was, kon 'n breedvoerige ondersoek nie uitgevoer word nie.

Die tokoferolinhoud van die olie is bepaal volgens die metode van Quaife en medewerkers⁸; die ru-olie bevat 7.4 mg. tokoferol/g. olie, terwyl die deur koolstof ontkleurde olie net 0.34 mg./g. bevat. Toetse vir sesamol en sesamolin was negatief⁹.

Samestellende vetsure van Maroela-olie

Die samestellende vetsure van Maroela olie is bepaal deur die distillasie van die metiel-esters van die suurgroepe wat verkry is uit kristallisasie by lae temperatuur volgens die metode wat gebruik is in die ondersoek van *Acacia cyclops*-olies¹⁰. Die vetsure is eers uit die droë eter by -40°C . gekristalliseer (10 ml. eter/g. suur). Die oplosbare vetsure is daarna omgekristalliseer uit asetoon (10 ml./g. suur) by -60°C . en die vetsure sodoende geskei in 'n eter-onoplosbare fraksie A, 'n asetoon-onoplosbare fraksie B en 'n asetoon-oplosbare fraksie C. (Tabel II). Elke groep vetsure is daarna omgesit in die metiel-esters wat gedistilleer is deur 'n elektries verwarmde en gepakte kolom onder verminderde druk¹¹. Fraksies met 'n jood getal hoër as 130 is onderwerp aan alkaliese isomerisasie volgens die metode van Mitchell, Kraybill en Zschiele¹² en spektrofotometries ondersoek by 234 en 268 $\text{m}\mu$ om die linolien en linoleensure te bepaal. Die besonderhede van die distillasies en die analises van die fraksies uit die drie ester groepe word in Tabelle III (a)-(c) aangegee.

Die teenwoordigheid van linoliensuur in die olie is soos volg bewys¹³. Een gram vetsuur van fraksie C₂ word in petroleum eter ($40-60^{\circ}\text{C}$.) opgelos en die oplossing tot onder 0° afgekoel. 'n Oplossing van 1g. broom in 5 ml. petroleumeter ($40-60^{\circ}\text{C}$.) word drupsgewys by die vetsuur-oplossing gevoeg en die temperatuur onder 0° gehou. Die wit presipitaat wat gevorm het, word afgefiltreer en die presipitaat omgekristalliseer uit etileendichloried. Opbrengs: 0.5 g., smeltpunt $113-114^{\circ}$, tetrabroomderivaat van linoliensuur, smeltpunt 114° wat geen verlaging in die mengsmeltpunt met dié uit fraksie C₂ aantoon nie.

Maroela olie bevat dus linoliensuur. Aangesien die broomverbinding 'n smeltpunt van $113-114^{\circ}\text{C}$. het, is aangeneem dat linoleensuur (heksabroomderivaat s.p. 180°C .) afwesig is¹⁴.

Die samestelling van die verskillende fraksies en die totale vetsure uit die olie is bereken volgens die metode van Hilditch¹⁵ met behulp van die vergelykings van Rapson en medewerkers¹⁶.

Die resultate word in Tabel IV opgesom.

Dit sal opgemerk word dat die huidige monster 'n baie hoër persentasie versadigde vetsure bevat as dié wat deur Jones⁴ ondersoek is (22.2 persent vergelyk met 7 persent) en 'n ooreenkomstige laer persentasie linolien en oliensure bevat. Dit is nie moontlik om te sê of hierdie verskil 'n werklike verskil in samestelling is nie en of dit te wyte is aan die huidige moderne en meer akkurate analitiese metodes om die samestelling van vetsure te bepaal.

TABEL II
Kristallisasie van die vetsure by 'n lae temperatuur

| | Gewig van Groep (g.) | Persent | J. G. | Linolien-suur persent | Linolien-suur persent |
|--|----------------------|---------|-------|-----------------------|-----------------------|
| (a) Onoplosbaar in eter (-40°) | 93.5 | 29.3 | 31.7 | 0.24 | — |
| (b) Onoplosbaar in aseton (-60°) | 196.4 | 61.7 | 88.9 | 2.74 | — |
| (c) Oplosbaar in aseton (-60°) | 28.5 | 9.0 | 136.3 | 56.0 | 2.36 |
| Totale vetsure | — | — | — | 6.4 | 0.42 |

TABEL III
Gefraksioneerde distillasie van die metiel esters van die vetsure van Groepe A, B en C
(a) Metiel esters van groep A

| Fraksie | Kookpunt | Gewig (g.) | V.E. | J. G. |
|---------|----------|------------|-------|-------|
| 1 | 111° | 6.8188 | 270.9 | 6.4 |
| 2 | 116° | 6.2080 | 268.7 | 4.2 |
| 3 | 130° | 6.3568 | 270.6 | 7.8 |
| 4 | 131° | 6.6895 | 276.8 | 21.8 |
| 5 | 135° | 5.8081 | 280.2 | 25.1 |
| 6 | 145° | 5.6576 | 278.5 | 27.0 |
| 7 | 145° | 6.2278 | 282.4 | 33.8 |
| 8 | 145° | 6.2766 | 286.5 | 42.1 |
| 9 | 145° | 6.6652 | 289.1 | 45.6 |
| 10 | 146° | 6.5341 | 292.7 | 47.6 |
| 11 | 147° | 6.2031 | 294.4 | 48.2 |
| 12 | 148° | 5.7309 | 294.0 | 47.5 |
| 13 | 149° | 5.9652 | 293.5 | 45.0 |
| 14 | 157° | 5.4596 | 292.7 | 37.0 |
| 15 | Res. | 3.8716 | 341 | 12.8 |

Totale gewig 90.4730

(b) Metiel esters van Groep B

| Fraksie | Kookpunt | Gewig (g.) | V.E. | J. G. |
|---------|----------|------------|-------|-------|
| 1 | 131° | 5.2342 | 284.5 | 60.1 |
| 2 | 135° | 6.7401 | 294.1 | 85.2 |
| 3 | 138° | 6.2989 | 293.7 | 86.4 |
| 4 | 140° | 6.1969 | 295.6 | 86.3 |
| 5 | 145° | 6.1817 | 295.2 | 87.3 |
| 6 | 150° | 5.7194 | 296.2 | 86.8 |
| 7 | 153° | 6.2131 | 294.6 | 87.5 |
| 8 | 154° | 6.0433 | 295.2 | 87.3 |
| 9 | 155° | 6.9952 | 293.2 | 87.1 |
| 10 | 155° | 6.1270 | 295.2 | 86.9 |
| 11 | 155° | 6.3844 | 294.9 | 87.5 |
| 12 | 155° | 5.9521 | 295.4 | 86.9 |
| 13 | 155° | 5.8773 | 295.9 | 86.9 |
| 14 | 155° | 5.9588 | 296.3 | 86.4 |
| 15 | Res. | 5.0390 | 304.9 | 76.9 |

Totale gewig: 90.9614

(c) Metieesters van Groep C

| Fraksie | Kookpunt | Gewig | V.E. | J.G. | Persent Linolien- suur | Persent Linoleen- suur |
|---------------|----------|---------|-------|-------|------------------------------|------------------------------|
| 1 | 142° | 5.1943 | 283.2 | 130.7 | — | — |
| 2 | 142° | 4.7731 | 289.7 | 146.7 | 64.6 | 1.02 |
| 3 | 142° | 4.4732 | 292.4 | 145.6 | 63.7 | 1.2 |
| 4 | 150° | 4.7790 | 294.8 | 143.2 | 59.7 | 1.4 |
| 5 | Res. | 7.0980 | 312.8 | 106.2 | — | — |
| Totale gewig: | | 26.3176 | | | | |

TABEL IV
Samestellende vetsure van Maroela olie

| Suur | Groep | | | Totale vetsure persent gewig |
|----------------------------------|---------|---------|---------|------------------------------------|
| | Groep A | Groep B | Groep C | |
| Palmitien | 13.1 | 3.0 | — | 16.1 |
| Stearien | 4.8 | 0.3 | — | 5.1 |
| C ₁₀ -versadig | 0.1 | — | — | 0.1 |
| C ₁₂ -versadig | 1.0 | — | — | 1.0 |
| Heksadekeen | — | — | 1.1 | 1.1 |
| Olien | 10.4 | 54.6 | 1.7 | 66.7 |
| Linolien (bereken) | — | 2.6 | 4.6 | 7.2 |
| Linoleen (bereken) | — | — | spoor | — |
| C ₂₀ -2H | — | 1.1 | 1.6 | 2.7 |
| Totaal | | | | 100.0 |

Volgens Hilditch¹⁷ is die hoofsure van saadodies van die Anacardiaceae-familie; palmitien, olien en linoliensure, en in 'n paar gevalle steariensuur. Volgens ons resultate is Maroela olie dus 'n verteenwoordigende olie van die Anacardiaceae-familie.

Maroela olie is 'n nie-droënde olie, en behoort eetbaar te wees indien dit op groot skaal geproduseer kan word. Die hoë tokoferol-inhoud van die ru-olie behoort die olie teen oksidasie te beskerm.

Hierdie artikel word gepuliseer met die toestemming van die Suid-Afrikaanse Wetenskaplike en Nywerheidsnavorsingsraad. Die skrywers wil verder hulle dank betuig jeens Dr. Rapson vir sy belangstelling in die werk en Mnr. J. H. Ligthelm, wie die pitte bymekaar gemaak het.

Ontvang 18 Julie, 1951

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THE ANODIC OXIDATION OF CALCIUM LACTATE SOLUTIONS

by

N. R. M. IMPEY and E. T. VERDIER

OPSOMMING

Die anodiese oksidasie van kalsium laktaat oplossings by 'n platina elektrode is ondersoek en die produkte van elektrolise is geïdentifiseer en bepaal.

SUMMARY

The anodic oxidation of calcium lactate solutions at a platinum electrode has been investigated and the products of electrolysis identified and estimated.

Ever since Kolbe¹ first observed in 1849 that hydrocarbons are evolved at the anode when the salts of a fatty acid are electrolysed, numerous workers have attempted to use his method for the synthesis of organic compounds. Walker², for example, endeavoured to obtain dihydric alcohols by electrolysing the corresponding salts of the hydroxy acids. This led him to study the electrolysis of a sodium lactate solution without, however, succeeding in isolating any butylene glycol.

Since then other workers³⁻⁷ have also studied the anodic behaviour of the lactate ion. While they agree with regard to the formation of acetic acid and acetaldehyde in the anode solution, and the liberation of carbon dioxide, oxygen and carbon monoxide, their results are in complete disagreement with respect to other compounds. Smull and Subkow³ reported the formation of formic acid and pyruvic acid, while Bradt and Fallscheer⁴ claim that neither of these is formed. Carpeniseaunu⁵, making use of a very sensitive test⁸ and working at very small current densities, identified pyruvic acid in the final anolyte solution. Finally von Miller and Hofer⁶, working at different concentrations of potassium lactate, and Tommila⁷, using alkaline solutions of sodium lactate, both found no trace of pyruvic acid but certain amounts of formic acid. The former also found crotonaldehyde, while the latter reported the existence of hydrogen, methane and ethane amongst the gases liberated, and a trace of formaldehyde in solution.

While most of these results were obtained under somewhat different conditions they seemed too conflicting to be explained merely by the relatively small differences of current density, temperature, or the nature of the electrolyte, especially as they were all obtained with the same type of platinum electrode. Thus though the primary object of this research had been to obtain lactic acid from calcium lactate by an electrolytic method, it was felt, when this had to be abandoned owing to the small yields of lactic acid, that the very nature of the results published on this subject warranted a fuller investigation of the reactions taking place at the anode.

Apparatus

The electrodes were made of platinum foil, and the cathode compartment was separated from the anode by a sintered glass diaphragm of suitable porosity (No. 4 pyrex). The anode compartment had a capacity of about 300 ml. while the cathode compartment was somewhat smaller. The cathode solution, when necessary, was replaced every two hours, as the formation of calcium carbonate on the cathode or porous pot increases the resistance of the cell.

A calcium lactate manufactured in South Africa was used throughout. This salt was

sufficiently pure to be used as such without recrystallization. All experiments unless otherwise stated were carried out with a solution approximately 0.1 M.

The applied voltage could be varied from 0 to 20 volts by means of two rheostats of 70 and 8.5 ohms each, while a voltmeter and an accurate ammeter, capable of reading a wide range of currents from 1.5 amperes to 0.5 microamperes, were placed in the circuit.

Identification and estimation of the products of electrolysis in solution

Aldehydes. The presence of an aldehyde was revealed by the strong red colour which a few millilitres of the anode solution gave on addition of 2 ml. of Schiff's reagent. The aldehyde was identified as acetaldehyde by the addition product formed with "Dimedone" (dimethyl dihydro resorcinol)⁹ which forms derivatives with the aldehydes having widely different melting points. The absence of even the slightest traces of formaldehyde was further shown by a polarographic analysis. Hence, contrary to the results of von Miller and Hofer⁶, and Tommila⁷, no crotonaldehyde or formaldehyde is formed during the electrolysis.

Quantitatively, acetaldehyde was determined by the volumetric method developed by Friedemann¹⁰, Donally¹¹, and Reynolds and Irwin¹², and slightly modified by us. The results obtained are not absolute and for solutions 0.01 to 0.004 Molar the amount found is 92 ± 2 per cent of that actually present. (Reynolds and Irwin¹² give 90 per cent as the factor for solutions 0.02 to 0.03 Molar). Nevertheless this method was found to be more suitable for our purpose than the gravimetric or polarographic methods.

Acids. Electrolysis was carried out with a current of about 60 m.a. with electrodes having a surface of 6 sq. cm. until the solution was approximately 0.25 N. with respect to acid. Repeated electrolyses were performed until one litre of solution had been obtained. Ordinary qualitative tests proving inconclusive, except to show the absence of oxalic and glycolic acids, the volatile acids were separated from the non volatile by a vacuum distillation.

The following fractions were thus obtained:

- (a) An aqueous distillate containing only water and acetic acid.
- (b) A waxy solid. This solid which itself could be further separated into two fractions, a viscous oil and a dark brown solid, was tested for other free acids. Crotonic acid was found to be absent. Pyruvic acid was identified by the method of Simon improved by Carpeniseaunu⁸ but it was not present to an extent greater than 1.6 per cent of the total acidity.
- (c) A viscous oil. This was identified as lactic acid by the addition product formed with phenacyl bromide. It was also shown not to contain any butylene glycol-2.3 which would be the product of the Kolbe type of electrolytic reaction. Even when more concentrated solutions of lactate were used no butylene glycol-2.3 was found, though an increase in concentration is usually favourable to the Kolbe reaction. The electrolysis in this case was carried out at 60° C. so as to permit the use of a 10 per cent solution.
- (d) A dark brown solid. With a colour reminiscent of burnt sugar this solid is sparingly soluble in water and alcohol. Its exact nature was not determined, but it is probably composed of the products resulting from the decomposition of lactic acid with the loss of water.

Quantitative determination of lactic and acetic acids

The accuracy of the above method of separating the acetic acid from the lactic acid, and the very small quantities of pyruvic acid, was tested out by distilling in vacuo solutions of calcium lactate containing known quantities of lactic and acetic acids in approximately the same proportions as encountered in the anode solution.

As shown in Table I the most satisfactory distillation occurred at a maximum bath temperature between 50 and 55° C. The following procedure was therefore adopted: the bath temperature was kept at 40° C. for the major portion of the distillation and only increased to 50° C. towards the end when this temperature was maintained until the temperature of the distillate had fallen to 22° C. The pressure was adjusted to enable the greater part of the aqueous fraction to be collected at a vapour temperature of 30 to 35° C.

TABLE I

| Max. bath temp. °C. | Lactic acid in g. equivs. $\times 10^3$ | | | Acetic acid in g. equivs. $\times 10^3$ | | | Total acid in g. equivs. $\times 10^3$ | | |
|------------------------------|--|-------|---------------------|--|-------|---------------------|---|-------|---------------------|
| | Theor- etical | Found | Percentage error | Theor- etical | Found | Percentage error | Theor- etical | Found | Percentage error |
| 45 | 4.94 | 5.02 | 1.6 | 1.12 | 1.01 | -10.0 | 6.06 | 6.03 | -0.5 |
| 45 | 4.94 | 5.01 | 1.5 | 1.12 | 1.02 | -9.3 | 6.06 | 6.02 | -0.6 |
| 50 | 4.94 | 4.94 | 0 | 1.12 | 1.07 | -3.1 | 6.06 | 6.01 | -0.7 |
| 50 | 4.94 | 4.91 | -0.7 | 1.12 | 1.07 | -3.1 | 6.06 | 5.98 | -1.3 |
| 55 | 4.27 | 4.19 | -1.9 | 1.14 | 1.14 | 0 | 5.42 | 5.34 | -1.2 |
| 55 | 4.27 | 4.18 | -2.4 | 1.17 | 1.17 | 2.7 | 5.42 | 5.35 | -1.2 |
| 60 | 4.46 | 4.39 | -1.5 | 0.62 | 0.66 | 6.4 | 5.08 | 5.05 | -0.6 |

Quantitative determination of pyruvic acid

Carpeniseaunu⁵ obtained pyruvic acid by the electrolysis of sodium lactate solutions at very small current densities. A prolonged electrolysis was therefore carried out with calcium lactate solutions under similar conditions. 350 ml. of a 0.12 Molar solution of calcium lactate were electrolysed for 290 hours at an applied voltage of 3.0 volts and a current of approximately 1 m.a. Under these conditions there was a slight evolution of gas at the cathode but almost none at the anode.

At the conclusion of the electrolysis the anode solution was found to be 0.00156 N. with respect to acid. 150 ml. of this solution was concentrated by vacuum distillation and the pyruvic acid determined colorimetrically⁶. The concentration of the undistilled solution was thus found to be 0.00145 N. It therefore appears that at low current densities over 90 per cent of the acid produced is pyruvic. It was further shown that at higher current densities (60 m.a. for the same electrodes with a surface of 6 sq. cm.), five times less pyruvic acid was found.

Gas analysis. Fig. 1 shows the apparatus used for this type of analysis. Special care was taken to ensure that all rubber to glass joints were air tight.

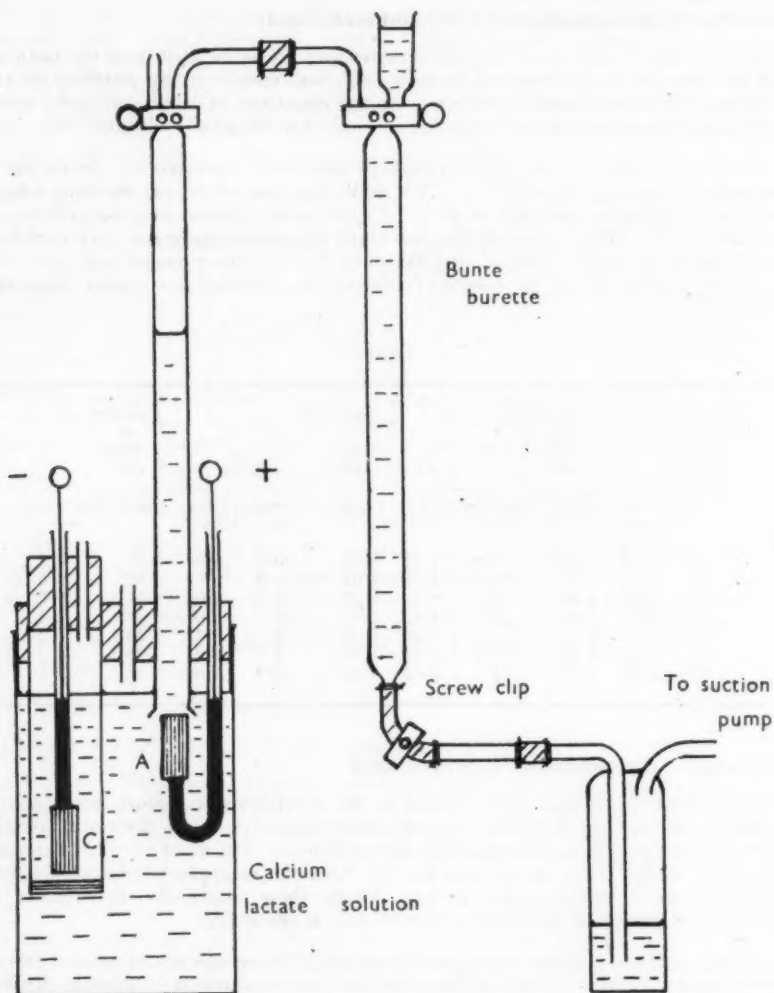


FIGURE 1. GAS COLLECTION

The gas which collected in the first burette was transferred, at the end of an electrolysis, to the Bunte burette and analysed in the usual way making use of the following absorbents:

A 30 per cent aqueous solution of KOH for carbon dioxide¹⁸.

A freshly prepared alkaline pyrogallol solution (4 volumes 40 per cent KOH to 1 volume 25 per cent pyrogallol) for oxygen.

Ammoniacal cuprous chloride for carbon monoxide. (125 ml. conc. HCl, 40 g. CuCl and 130 ml. conc. ammonia.)

A solution of bromine in 10 per cent potassium bromide for hydrocarbons.

Preliminary results revealed the presence of oxygen, carbon dioxide, a trace of carbon monoxide, no hydrocarbons and a certain amount of residual gas (10 per cent of the total volume) which proved to be nitrogen. If the electrolyte was saturated with oxygen the volume of this residual gas was considerably reduced. As the amount increased with the time of electrolysis and the total volume of gas, it must be presumed that this nitrogen was simply removed from the solution. A similar effect was reported by Shukla and Walker¹⁴ during the electrolysis of acetates.

The trace of carbon monoxide was shown to result from the tendency of the alkaline pyrogallol to evolve carbon monoxide on absorption of oxygen. This effect, which has been reported by Drakeley and Nicol¹⁵, was confirmed by using alkaline sodium hyposulphite as the absorbent for oxygen, when it was found that the amount of carbon monoxide was completely negligible. However, as pyrogallol absorbs oxygen more quickly than the hyposulphite, it was used for all analysis, and the volume of carbon monoxide formed simply added to the volume of oxygen.

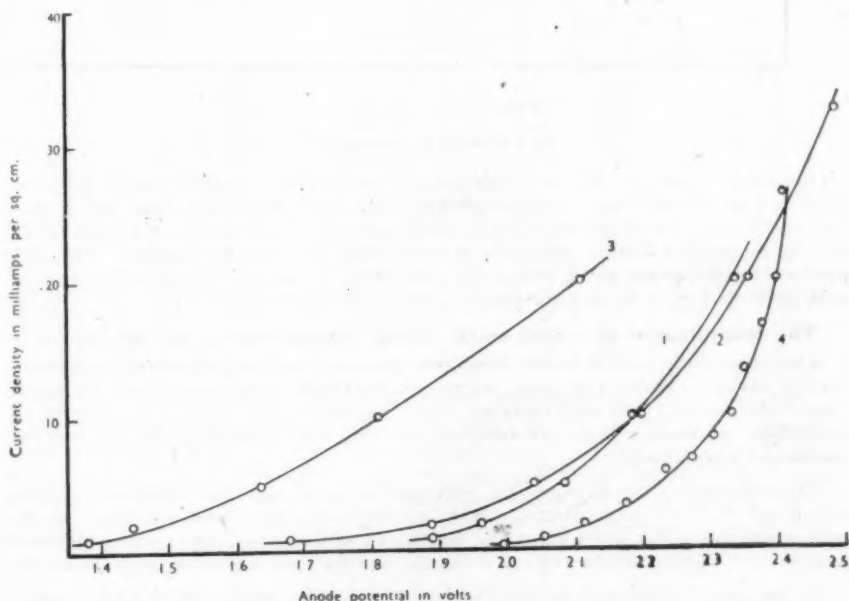


Fig. 2. Curve 1: 0.1 M. calcium lactate solution.

Curve 2: 0.1 M calcium lactate solution 0.01N with respect to sodium hydroxide.

Curve 3: 0.01 M sodium hydroxide solution.

Curve 4: 0.1 M calcium lactate solution 0.02 M with respect to hydrogen ions.

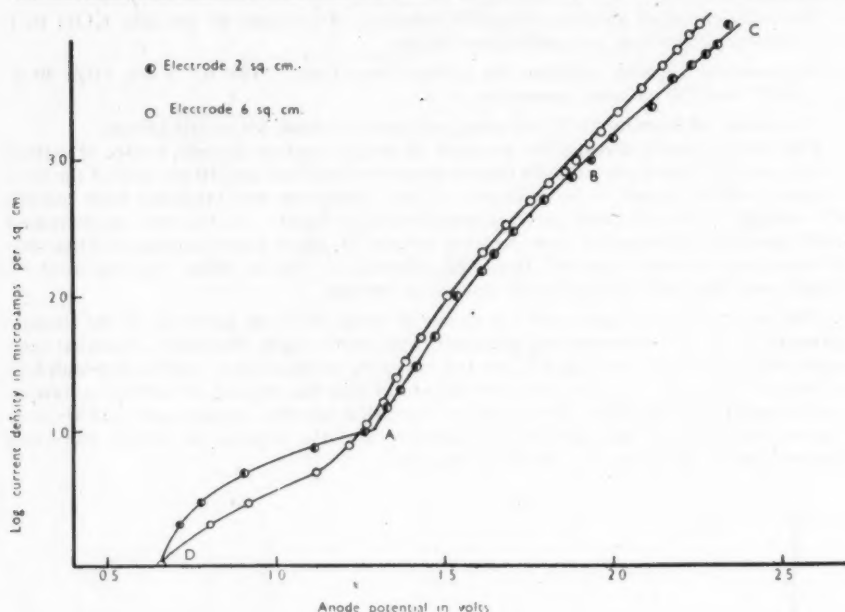


Fig. 3. 0.1 M calcium lactate solution.

One might conclude that the small amounts of carbon monoxide which previous workers have found^{6, 8} are, in all probability, due to this effect more especially as they state that the amount of carbon monoxide increased with the percentage of oxygen which is to be expected if alkaline pyrogallol is used as the absorbent for oxygen. The only products formed at the anode during the electrolysis of calcium lactate are thus: acetic acid, lactic acid, pyruvic acid, acetaldehyde, oxygen and carbon dioxide.

The determination of current anode voltage/current density voltage curves

A tool frequently used to study electrolytic reactions is to plot, anode voltage-current density, curves. These, if properly interpreted, shed light on the actual reactions occurring at the anode. It is such evidence which has shown that in the vast majority of electrolytic reactions in aqueous solutions, no ions other than the hydroxyl ions are discharged at the anode.

The electrolysis of acetates has received a good deal of attention in this direction^{14, 16, 17, 18, 19} and definite breaks in the curve have been attributed to the commencement of the Kolbe reaction. In the case of the lactate ions it was hoped that inflexion in the curve might give some indication of the reactions occurring at the anode.

In this investigation the curves were obtained by the direct method which merely consists in measuring the potential of the anode at different values of the polarizing current. The potential of the anode was determined with respect to a saturated calomel electrode.

TABLE II

| Electrolysis No. | Current in milliamps. | Time in mins. | Total acid in g. equivs. $\times 10^3$ | Acetic acid in g. equivs. $\times 10^3$ | Lactic acid in g. equivs. $\times 10^3$ | Acetaldehyde in g. equivs. $\times 10^3$ | Total gas in cc. at N.T.P. | Carbon dioxide in g. equivs. $\times 10^3$ | Oxygen in g. equivs. $\times 10^3$ |
|---------------------------------|-----------------------|---------------|--|---|---|--|----------------------------|--|------------------------------------|
| <i>Electrode Area 2 sq. cm.</i> | | | | | | | | | |
| 1 | 10 | 1200 | 4.17 | 0.88 | 3.14 | 1.14 | 13.0 | 0.14 | 1.38 |
| 2 | 20 | 510 | 3.99 | 0.80 | 3.01 | 0.98 | 16.2 | 0.29 | 1.36 |
| 3 | 20 | 510 | 4.34 | 0.86 | 3.16 | 1.00 | 14.6 | 0.29 | 1.21 |
| 4 | 20 | 510 | 4.15 | — | — | 0.96 | 15.3 | 0.35 | 1.10 |
| 5 | 40 | 470 | 6.36 | 1.09 | 5.09 | 1.37 | 20.3 | 0.22 | 2.28 |
| 6 | 40 | 428 | 5.58 | 1.11 | 4.27 | 1.53 | 20.2 | 0.23 | 2.22 |
| 7 | 40 | 300 | 4.80 | 0.99 | 3.24 | 1.26 | 24.2 | 0.58 | 1.36 |
| 8 | 50 | 420 | 6.96 | 1.48 | 5.40 | 1.52 | 29.5 | 0.46 | 2.91 |
| 9 | 50 | 420 | 6.68 | 1.60 | 4.83 | 1.90 | 20.6 | 0.26 | 2.23 |
| 10 | 50 | 420 | 7.06 | 1.45 | 5.40 | 1.70 | 27.0 | 0.42 | 2.68 |
| 11 | 60 | 270 | 5.81 | 1.12 | 4.27 | 1.44 | 28.5 | 0.65 | 2.16 |
| 12 | 60 | 270 | 6.43 | 1.32 | 4.73 | 1.47 | 24.5 | 0.50 | 2.02 |
| 13 | 60 | 270 | 5.98 | 1.41 | 4.29 | 1.23 | 20.9 | 0.28 | 2.23 |
| 14 | 60 | 270 | 5.05 | 1.20 | 3.82 | 1.47 | 17.6 | 0.25 | 1.77 |
| 15 | 70 | 270 | 7.70 | 1.36 | 6.17 | 1.58 | 27.9 | 0.57 | 2.29 |
| 16 | 80 | 160 | 4.75 | 0.96 | 3.50 | 1.19 | 31.3 | 0.96 | 1.51 |
| <i>Electrode Area 6 sq. cm.</i> | | | | | | | | | |
| 17 | 10 | 1200 | 4.80 | 0.53 | 4.27 | 0.30 | 27.4 | 0.13 | 3.87 |
| 18 | 20 | 510 | 4.81 | 0.51 | 4.06 | 0.33 | 31.0 | 0.43 | 3.36 |
| 19 | 20 | 510 | 4.87 | 0.61 | 4.12 | 0.33 | 27.4 | 0.35 | 3.10 |
| 20 | 20 | 510 | 4.81 | 0.65 | 4.01 | 0.34 | 33.1 | 0.58 | 3.24 |
| 21 | 40 | 390 | 5.84 | 0.97 | 4.87 | 1.02 | 31.2 | 0.23 | 4.06 |
| 22 | 40 | 450 | 6.56 | 0.89 | 5.42 | 1.41 | 33.9 | 0.28 | 4.41 |
| 23 | 40 | 415 | 6.04 | 0.91 | 4.94 | 1.18 | 26.4 | 0.18 | 3.48 |
| 24 | 40 | 300 | 5.42 | 0.87 | 4.30 | 0.78 | 42.0 | 0.98 | 3.21 |
| 25 | 50 | 420 | 7.77 | 1.14 | 6.38 | 1.44 | 41.3 | 0.47 | 4.97 |
| 26 | 50 | 420 | 7.72 | 1.20 | 6.34 | 1.63 | 31.5 | 0.24 | 4.15 |
| 27 | 50 | 420 | 7.75 | 1.24 | 6.36 | 1.75 | 37.9 | 0.43 | 4.45 |
| 28 | 60 | 270 | 6.50 | 0.85 | 5.21 | 1.36 | 40.1 | 0.78 | 3.63 |
| 29 | 60 | 270 | 7.19 | 1.04 | 5.77 | 1.45 | 35.9 | 0.62 | 3.46 |
| 30 | 60 | 270 | 5.32 | 1.18 | 4.33 | 1.29 | 26.2 | 0.23 | 3.28 |
| 31 | 70 | 270 | 7.71 | 1.09 | 6.69 | 1.19 | 39.8 | 0.54 | 4.45 |
| 32 | 70 | 250 | 6.55 | 1.30 | 4.90 | 1.36 | 31.9 | 0.69 | 2.59 |
| 33 | 80 | 160 | 4.87 | 0.79 | 4.01 | 1.05 | 41.6 | 1.11 | 2.70 |

Fig. 2 and 3 show some of the results obtained, in the first case for current densities ranging from 1 to 25 m.a./sq. cm. and in the second case from 10 m.a./sq. cm. down to 1 μ a./sq. cm. The curves in Fig. 2 give no indication of any changes in the reaction at the anode which might result from a variation of the applied voltage. A gradual increase of the anode voltage with time of electrolysis was noticed. This is due to the decrease in the pH of the solution as is shown by the curve 4. (Calcium lactate solution 0.02 N. with respect to acid.)

Curve 1 (calcium lactate solution) and curve 2 (Calcium lactate solution 0.01 N. with respect to NaOH) lie close together and therefore it can be assumed that the fundamental electrolytic reactions are the same in both cases. Curve 3 (0.01

N — NaOH) is displaced to the left, and this would indicate that in the presence of lactate ions the secondary oxidation processes are different to those occurring in a sodium hydroxide solution. A similar case has been reported by Glasstone and Hickling¹⁹ when studying the electrolysis of 2 N. potassium acetate, alone, and in the presence of 0.01 N — NaOH. In both cases the anode voltage was found to be well above the evolution potential for oxygen.

The curves in Fig. 3 may be divided into three distinct sections. The portion DA was the least reproducible but the general shape is similar to that obtained by Audubert and Verdier²⁰ for sodium hydroxide solutions. The section AB probably corresponds to the formation of pyruvic acid the yield of which is greatest in this region, while the almost linear section BC corresponds to the first part of the curves in Fig. 2.

TABLE III

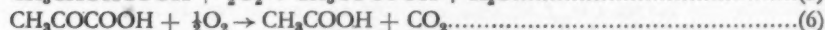
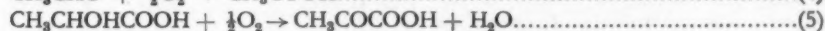
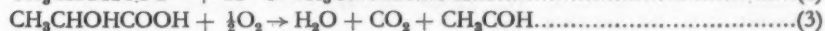
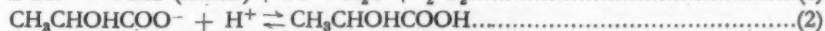
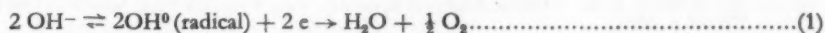
| <i>Electrolysis No.</i> | <i>No. of Faradays x 10³</i> | <i>A g. equivs. oxygen per Faraday</i> | <i>B g. equivs. acetaldehyde per Faraday</i> | <i>C g. equivs. acetic acid per Faraday</i> | <i>A+2B+4C</i> |
|-------------------------|---|--|--|---|----------------|
| 1 | 7.5 | 0.185 | 0.153 | 0.118 | 0.963 |
| 2 | 6.3 | 0.216 | 0.156 | 0.127 | 1.036 |
| 3 | 6.3 | 0.192 | 0.159 | 0.137 | 1.058 |
| 4 | 6.3 | 0.175 | 0.152 | — | — |
| 5 | 11.9 | 0.205 | 0.122 | 0.115 | 0.909 |
| 6 | 10.6 | 0.209 | 0.144 | 0.104 | 0.913 |
| 7 | 7.5 | 0.182 | 0.168 | 0.133 | 1.050 |
| 8 | 13.1 | 0.227 | 0.116 | 0.113 | 0.911 |
| 9 | 13.1 | 0.171 | 0.146 | 0.123 | 0.955 |
| 10 | 13.1 | 0.205 | 0.130 | 0.111 | 0.909 |
| 11 | 10.1 | 0.215 | 0.143 | 0.111 | 0.945 |
| 12 | 10.1 | 0.201 | 0.146 | 0.131 | 1.017 |
| 13 | 10.1 | 0.222 | 0.122 | 0.140 | 1.026 |
| 14 | 10.1 | 0.176 | 0.146 | 0.119 | 0.944 |
| 15 | 11.8 | 0.195 | 0.134 | 0.116 | 0.927 |
| 16 | 8.0 | 0.190 | 0.150 | 0.121 | 0.974 |
| 17 | 7.5 | 0.519 | 0.040 | 0.071 | 0.883 |
| 18 | 6.3 | 0.533 | 0.052 | 0.081 | 0.961 |
| 19 | 6.3 | 0.492 | 0.054 | 0.097 | 0.988 |
| 20 | 6.3 | 0.514 | 0.054 | 0.103 | 1.034 |
| 21 | 9.7 | 0.418 | 0.105 | 0.100 | 1.028 |
| 22 | 11.9 | 0.395 | 0.126 | 0.080 | 0.967 |
| 23 | 10.3 | 0.337 | 0.114 | 0.088 | 0.917 |
| 24 | 7.5 | 0.430 | 0.105 | 0.117 | 1.108 |
| 25 | 13.1 | 0.381 | 0.110 | 0.087 | 0.949 |
| 26 | 13.1 | 0.318 | 0.125 | 0.092 | 0.936 |
| 27 | 13.1 | 0.341 | 0.134 | 0.095 | 0.989 |
| 28 | 10.1 | 0.361 | 0.135 | 0.084 | 0.967 |
| 29 | 10.1 | 0.344 | 0.144 | 0.103 | 1.044 |
| 30 | 10.1 | 0.326 | 0.128 | 0.108 | 1.014 |
| 31 | 11.8 | 0.378 | 0.101 | 0.093 | 0.952 |
| 32 | 10.9 | 0.349 | 0.132 | 0.064 | 0.869 |
| 33 | 8.0 | 0.340 | 0.132 | 0.099 | 1.000 |

DISCUSSION

Table 2 gives a complete list of the results obtained for electrolyses carried out at different current intensities, while Table III gives some of the results that may be deduced from these values. No mention is made in these tables of pyruvic acid as it is only formed at current densities much inferior to those given in the table.

Two main theories have been put forward to explain the mechanism of the anode reactions during the electrolysis of solutions of fatty acids. According to the theory proposed by Crum Brown and Walker²¹ the anions of the organic acid are discharged alone or simultaneously with hydroxyl ions at the anode. However, if the acid anions are discharged preferentially to the hydroxyl ion, this reaction should occur at a lower voltage. A consideration of current-voltage curves has shown that this is not the case. To get round this difficulty Glasstone and Hickling¹⁹ put forward the hydrogen peroxide theory. This theory postulates that only hydroxyl ions are discharged at the anode, the OH radicals uniting irreversibly to form hydrogen peroxide which oxidizes the free acid or its anion in solution. While this represented a definite advance on the previous theory, recently Hickling²² has admitted, as a result of the work of Haissinsky and Cottin²³ that it cannot be considered as really satisfactory. Thus, at present, no explanation can be given as to why the oxygen overvoltage is so much greater in the presence of an organic radical than in its absence. (See current-voltage curves obtained in this investigation). Adam²⁴ has made the suggestion that this might well be due to a crowding out effect but, in the absence of definite proof, the matter is still open for discussion.

While no conclusion on this problem may be deduced from our results, nevertheless they would seem to indicate that the primary process at the anode is, in accordance with the theory of Glasstone and Hickling, the discharge of hydroxyl ions alone. Assuming this, the following reactions should take place at the anode during the electrolysis of calcium lactate solutions:



The solution would thus become more acid during electrolysis, while the formation of each molecule of acetaldehyde would be accompanied by the disappearance of two equivalents of oxygen, and every molecule of acetic acid by four equivalents. If these equations correctly represent the reactions taking place it should be possible to compare the total amount of oxygen formed with that liberated by the number of coulombs sent through the solution. The last column of Table III shows that the results bear out the theory within the degree of accuracy of the determination.

It should be noted that the determination of acetic acid is the least reliable and that any error in this estimation is therefore multiplied by a factor of four. Further at small current densities a deviation from the theoretical value is to be expected, owing to the formation of pyruvic acid which would be oxidized to acetic acid without passing through the intermediate stage of acetaldehyde²⁵. This is born out by the fact that the yield of acetaldehyde falls off at low current densities, while that of acetic acid remains almost constant.

It would therefore appear from a consideration of these results and of the current voltage-curves, that in the case of calcium lactate solutions, as for most anodic discharge processes, with the exception of the halogens and assimilated ions, only hydroxyl ions are discharged at the anode.

Acknowledgements

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THE NITRIC ACID OXIDATION OF COAL

PART III. INVESTIGATION OF A CHROMATOGRAPHICALLY SEPARATED NITROHUMIC ACID FRACTION

by

B. L. VAN DUUREN

OPSOMMING

'n Uitvoerige chemiese ondersoek van 'n nitrohumiezuurmengsel verkry deur die nitrohumiezuurmengsel op sellulose te kromatografeer (Deel II) word beskrywe. Die gevolgtrekkings wat op grond van die eksperimentele resultate gemaak is word bespreek. Karboksiel- en hidroksielgroepe is bepaal, die aard van die stikstof ondersoek, en die teenwoordigheid van heterosikliese suurstof word aangedui.

SUMMARY

A detailed chemical investigation of a nitrohumic acid fraction, obtained by chromatographing the nitrohumic acid mixture on cellulose (Part II), is described. The conclusions drawn from the experimental results are discussed. Carboxyl- and hydroxyl groups were determined, the nature of the nitrogen investigated and the presence of heterocyclic oxygen indicated.

In a previous communication¹ the chromatographic separation of the ether-insoluble

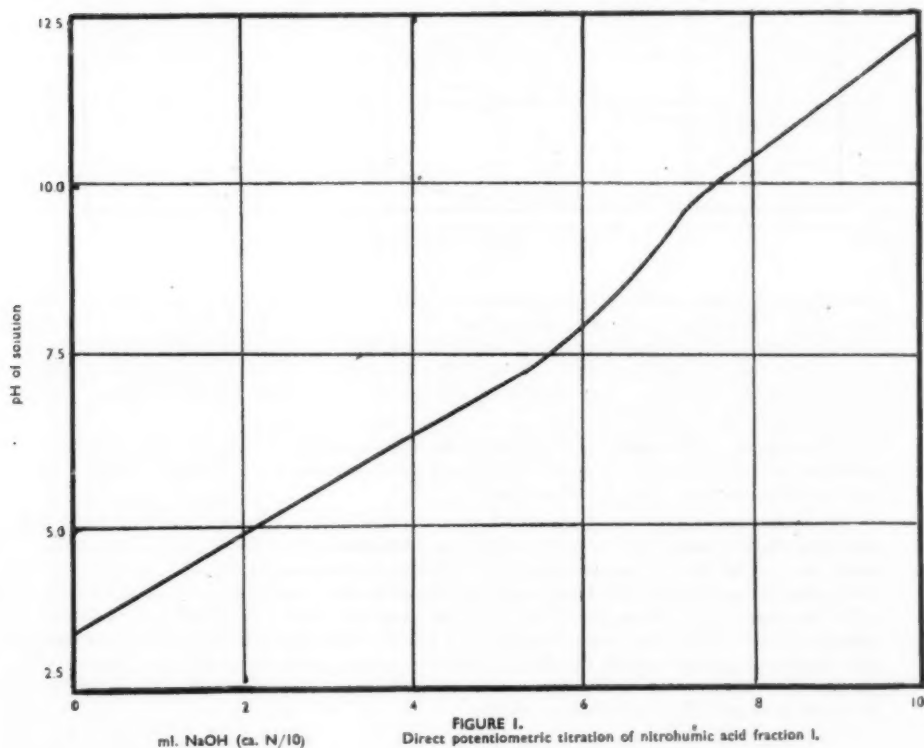


FIGURE 1.
Direct potentiometric titration of nitrohumic acid fraction I.

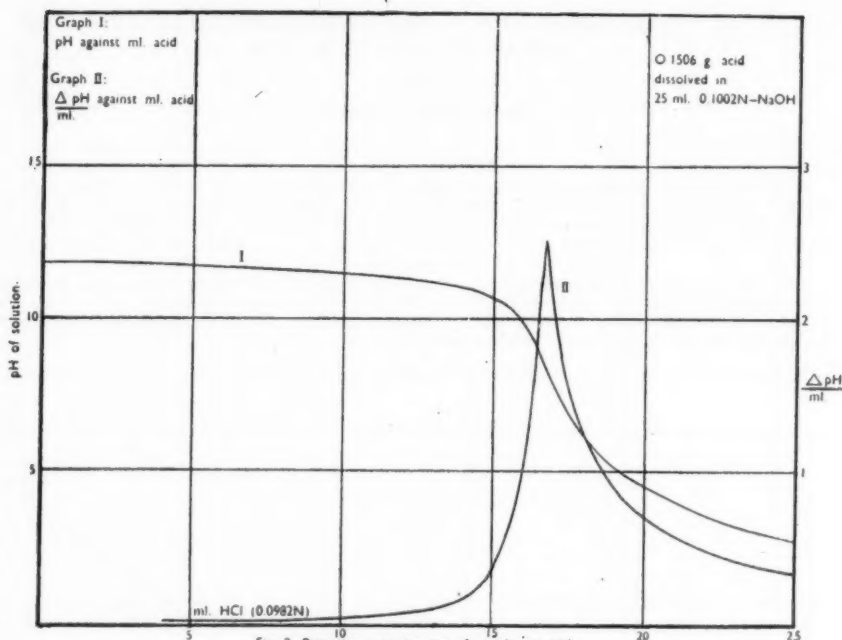


Fig. 2. Potentiometric titration of nitrohumic acid fraction for equivalent weight determination

fraction of the nitric acid oxidation product of coal into five fractions, on cellulose, was described. Fraction I, constituting about one-half of the ether-insoluble mixture, has now been obtained in larger quantities by a method of fractional precipitation from an acetone solution with ether. A number of experiments were performed on this acetone-soluble fraction. The analysis of this product was very similar to that of the chromatographic fraction I.

Although no claim could be made as to the homogeneity of this product, since no criterion of purity existed, the results from such an investigation are of greater value than any investigations on the original mixture.

The equivalent weight was determined potentiometrically. By direct titration against standard alkali a curve with a gentle slope was obtained so that no deduction could be made except that the substance under investigation is a weak acid, Fig. 1. In order to determine the equivalent weight an excess of standard alkali was added and back-titrated, with the glass electrode in the system, against standard acid. A value of 174.1 was obtained for the equivalent weight of the acid, Fig. 2. No distinction between carboxyl and hydroxyl groups could be made. Similar curves were obtained by Fuchs and Sandhoff². The results of the equivalent weight determination are discussed further in connexion with the methylation results.

The extinction curves for the acid were constructed in both ultraviolet- and visible

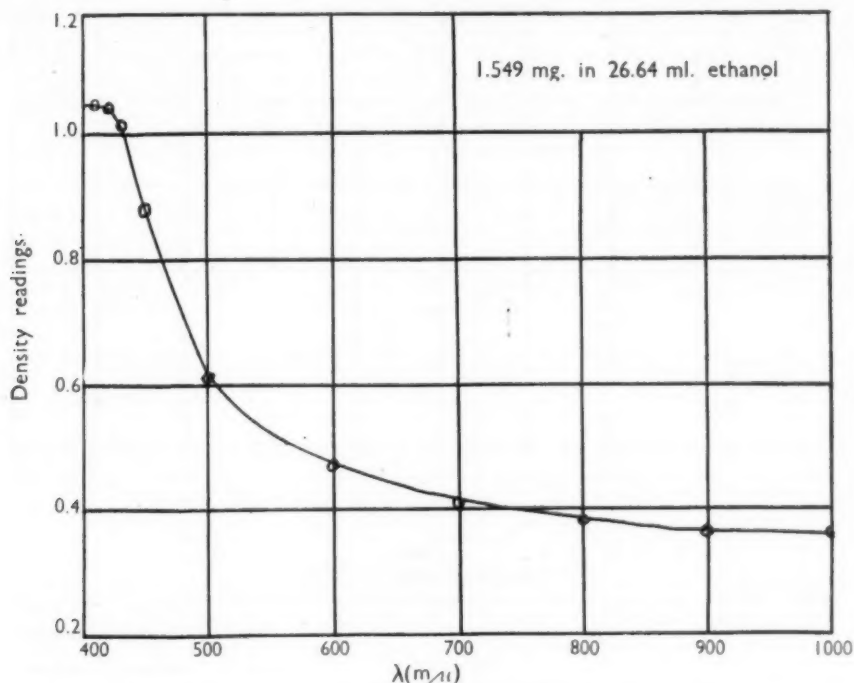


Fig 3 Extinction curve of nitrohumic acid fraction I in visible light

light, with absolute ethanol and with aqueous alkali as solvents for both sources of light. The results were disappointing in that in all cases the same general trend of decreased density with increased wave length was found, Fig. 3 and 4. From this latter fact it was concluded that no characteristic chromophoric groups are present. It is interesting to note that similar curves were obtained by Thiessen and Engelder³.

The nature of the oxygen

The oxygen in humic acid occurs in various forms. Thus the presence of hydroxyl- and carboxyl groups have been proved beyond doubt⁴. Carbonyl groups have been found to be present in some humic acids⁵. Heterocyclic- and linear ether oxygen has been regarded as accounting for a large fraction of the oxygen in humic acids. The difficulty of accounting for the oxygen in humic acids is increased, in the case of the nitrohumic acids, as a result of the fact that a portion of the oxygen will be present in nitrogen-containing structures. The evidence obtained from the various experiments described in the present investigation is as follows:—

(i) **Carboxyl and hydroxyl groups.** These groups were determined by various methods of methylation. The results are presented in Table I.

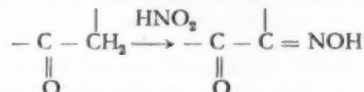
(ii) **The determination of carbonyl groups** in humic acids has received the attention of various workers⁵. In the present investigation, it was decided not to attempt the preparation of oximes, etc. in view of the difficulties that would attend such preparation with complex amorphous starting materials. Indirect evidence pointing to the absence of carbonyl groups as such was, however, obtained from various experiments:—

1. Reduction with aluminium-isopropoxide which would indicate the presence of carbonyl groups if acetone is obtained in the distillation product:—

$$R_1R_2CO + (CH_3)_2CHO)_3Al \rightarrow (R_1R_2CHO)_3Al + (CH_3)_2CO.$$

(Meerwein-Ponndorf-Verley Reduction). No acetone could be detected in the distillate. It should be noted, however, that this method cannot be applied to highly enolic ketones, e.g. β diketones or β ketonic esters.

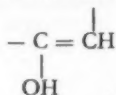
2. Reaction with nitrous acid: Ketomethylene groups, if present, should react with nitrous acid to form the corresponding isonitrosoketone:—



The acid under investigation was therefore treated with nitrous acid under the correct conditions. The analytical results indicated that such a reaction had not taken place:

| | | | | C | H | N |
|------------------|-----|-----|-----|-------|------|------|
| Reaction product | ... | ... | ... | 50.22 | 3.34 | 3.62 |
| Original acid | ... | ... | ... | 50.86 | 2.99 | 4.13 |

It may be suggested that, if keto groups are present, they are in such structures as favour the enolization of the ketone and stabilization of the enol structure:



Such a state of affairs would also account for the presence of alcoholic hydroxyl groups, as is suggested by the results of the equivalent weight determinations and methylations. Stabilization of the enol structure would be possible in a molecule with conjugated double bonds, e.g., an aromatic ring in which resonance stabilization might participate.

(iii) **Heterocyclic and linear ether oxygen.** The experiments on the mixture of nitrohumic acids¹ did not supply much information regarding the nature of the heterocyclic and/or linear ether oxygen in the humic acids. It appears from methylation results that a large proportion of the oxygen of humic acids occurs in these structures. Fuchs⁶ found that when lignin or humic acids were treated with methyl glycol (i.e., the monomethyl ether of ethylene glycol), products were obtained which contained methoxyl groups. Analysis of the potassium salts of the products indicated that the reagent did not cause methylation.

The methyl glycol reaction product of the nitrohumic acid under investigation gave on analysis the following results:—

Analysis: C, 45.26; H, 3.28; N, 2.57.

Atomic Ratio: C, 1.0; H, 0.86; N, 0.047; O, 0.80.

The same product contained 6.52 per cent methoxyl.

Assuming a formula $C_{60}H_{40}N_4O_{38}$ (molecular weight: 1424) for the starting material these results suggest that the product contained the reacted portion of four molecules of methyl glycol. Fuchs⁶ found that two molecules of methyl glycol enter the humic acid molecule, assuming a molecular weight of 1400 for the humic acid.

Qualitative evidence for the presence of heterocyclic oxygen was obtained from a study of the nature of the nitrogen in the nitrohumic acid under investigation.

Decarboxylation experiments were performed on the mixed nitrohumic acids.¹ The results indicated that condensation reactions may have taken place since an insoluble, infusible amorphous product was obtained. In repeating the experiment on the pure fraction, phenol was added, since it is known that this substance has an inhibiting effect in such condensation reactions. Two products were obtained, viz.:

- (a) An amorphous light-brown methyl ethyl ketone-soluble substance (I).
- (b) An amorphous dark-brown insoluble substance, soluble in pyridine (II).

Therefore it appeared that the phenol had had some effect in retarding the condensation reaction. The results of this experiment, which have a bearing on the heterocyclic oxygen in the nitrohumic acid were discussed further in connexion with the graphical-statistical method of analysis.¹⁰ On methylation product I contained 9.30 per cent methoxyl and product II 5.92. Therefore, it appears that at least a portion of the hydroxyl hydrogen atoms are retained.

The nature of the nitrogen

Very little is known concerning this aspect of humic acid chemistry. The problem is complicated by the fact that the nature of the nitrogen differs from one humic acid preparation to the next, the greatest differences being noticed between humic acids prepared by the nitric acid oxidation of coal and those obtained by other methods of investigation.

The extent of the problem will be realized if it is remembered that in no case has all the nitrogen, as determined by the Dumas combustion method, been accounted for completely in heterocyclic- and linking nitrogen or in nitrogen present in functional groups. The nature of the nitrogen in the nitrohumic acid fraction was determined by various methods:—

(a) *Determination of the nitrogen liberated as ammonia by hydrolysis, oxidation and reduction.* Various procedures were followed:—

- Procedure I. (a) Alkaline reduction with zinc dust.
(b) Alkaline oxidation with potassium permanganate.
(c) Alkaline reduction with zinc dust.
- Procedure II. (a) Reduction with zinc dust and hydrochloric acid.
(b) Step (b) of Procedure I.
(c) Step (c) of Procedure I.
- Procedure III. (a) Alkaline oxidation with potassium permanganate.
(b) Reduction with zinc dust and alkalis.

The results obtained by the various procedures are presented in table II.

(b) *Analysis of the alkali-treated humic acid.* The product obtained by prolonged boiling of the nitrohumic acid with alkali was analysed for carbon, hydrogen and nitrogen. Comparison of the analytical results with those on the original product indicates that a slight loss in nitrogen (8.95 per cent of the total nitrogen) had occurred:—

| | | C | H | N |
|---------------------------|-----|-------|------|------|
| Alkali-treated humic acid | ... | 51.02 | 3.06 | 3.76 |
| Original nitrohumic acid | ... | 50.86 | 2.99 | 4.13 |

TABLE II

Nitrogen evolved as ammonia and nitrate by various reactions on nitrohumic acid fraction I.

| Procedure | Percentage of total nitrogen recovered as | | | | Percentage of total nitrogen recovered |
|-----------|---|---------------------------|-------------------------------|-------------------------------|--|
| | Ammonia by alkaline reduction | Ammonia by acid reduction | Ammonia by alkaline oxidation | Nitrate by alkaline oxidation | |
| 1 | 13.0 | — | 33.9 | 10.5 | 57.4 |
| 2 | — | 13.7 | 30.9 | 11.7 | 56.3 |
| 3 | — | — | 18.9 | 14.4 | 33.3 |

(c) *Analysis of the reduction products.* Reduction experiments on the mixture of nitrohumic acids¹ indicated that a loss of nitrogen takes place during reduction with various reagents. The fraction under investigation was therefore subjected to reduction with various mild reducing agents. The results are given in Table III.

The reduction products were found to be darker in colour than the original acid. An interesting feature was the tendency of the reduction products to form organic-solvent insoluble complexes with metallic salts (zinc- and titanium salts).

TABLE III

Analyses of reduction products of nitrohumic acid fraction I.

| Method of reduction | Percentages | | |
|--|-------------|----------|----------|
| | Carbon | Hydrogen | Nitrogen |
| 1. Titanous chloride | 57.35 | 4.08 | 1.23 |
| 2. Zinc amalgam and hydrochloric acid | 50.33 | 4.15 | 1.94 |

The reduction product from method 2 in Table III was treated with nitrous acid and the diazotized product hydrolysed with boiling ethanol. The resulting product contained 1.62 per cent nitrogen, i.e., a loss of 7.74 per cent nitrogen of the total nitrogen of the original unreduced acid had occurred.

(d) *Kjeldahlization.* This experiment afforded very little information regarding the nature of the nitrogen in the nitrohumic acid. Only 1.93 per cent of the total nitrogen (as obtained by the Dumas combustion method) could be obtained as ammonia by "Kjeldahlization". Similar results were obtained by Beet⁷ in investigations on the "Kjeldahlization" of coal. Beet indicated that heterocyclic nitrogen resists decomposition by sulphuric acid. Nitro-nitrogen may also not be recovered by "Kjeldahlization."

In interpreting the results of the investigations it will not be out of place to refer to the experiments of Charmbury *et al.*⁸. These workers determined the amount of ammonia evolved by various procedures. Their results are reproduced in Table IV.

TABLE IV

Nitrogen evolved as ammonia and nitrate by various reactions on a nitrohumic acid⁸

| Procedure | Percentage of total nitrogen evolved as | | | | Percentage of total nitrogen recovered |
|-----------|---|-------------------------------|-------------------------------|-------------------------------|--|
| | Ammonia by alkaline hydrolysis | Ammonia by alkaline reduction | Ammonia by alkaline oxidation | Nitrate by alkaline oxidation | |
| I | — | — | 21.9 | 68.4 | 90.3 |
| II | 22.3 | 23.7 | 45.6 | 4.2 | 95.8 |

From their results they concluded that the nitrogen is present in at least two forms:—

(a) A reduced state (21.9 per cent), i.e., nitroso- or isonitroso groups.

(b) A higher state of oxidation (68.4 per cent) probably nitro groups.

They also noted that a part of the nitro groups behaved differently on reduction because 23.7 per cent was reduced and evolved as ammonia while 45.6 per cent remained in the humic acid and was liberated as ammonia by alkaline permanganate. The elimination of only a part of the nitrogen present by alkaline reduction indicates that the nitro groups either occupy different positions in the humic acid molecule or that the reduction takes a different course at some intermediate stage.

In a later paper⁹ the same authors performed a similar series of experiments on known nitrogen-containing compounds. These results indicated that in no case is the nitrogen evolved quantitatively by the mode of treatment which one would expect to produce such results. Usually, however, the greater part of the nitrogen present in one type of group is liberated as ammonia or nitrate by that treatment which would normally be expected to split the group in question.

In view of these considerations it becomes clear that the results obtained in the present investigation have no strictly quantitative significance.

Qualitatively the presence of nitro groups is proved beyond doubt by:—

- Loss of nitrogen as nitrate by alkaline permanganate oxidation.
- Diazotization and hydrolysis of the reduced product (causing a loss of 7.74 per cent of the total nitrogen present in the nitrohumic acid).
- The dark colour of the reduced product (pointing to reduction of aromatic nitro- to amino-groups).

From the results of procedure 1 (Table II) a value of 44.4 per cent is obtained for the percentage of the total nitrogen present as nitro groups. A portion of the nitrogen eliminated as ammonia by the alkaline or acid reduction (procedures 1 and 2 respectively) may originate from nitro groups which were reduced and split off as ammonia. (The reduction would be expected to lead through intermediate stages at which ammonia is readily split off.) The low value for the percentage of nitrogen present as nitro, as obtained by reduction, diazotization and hydrolysis, indicates, like the results of Charm-bury *et al.*⁸, that the nitro groups occupy different positions or that during reduction, the reaction takes a different course.

The presence of nitroso and/or isonitroso groups is deduced qualitatively from:

- (a) The loss of nitrogen (8.95 per cent of the total nitrogen of the nitrohumic acid) by alkaline hydrolysis.
- (b) The loss of nitrogen (18.9 per cent of the total nitrogen of the nitrohumic acid) by alkaline permanganate oxidation.

From these results an approximate value for the percentage nitrogen present in either of these structures can be set at 18.9 per cent. The presence of nitroso groups is only presumed in view of the results of experiments in connexion with the oxygen functions of the nitrohumic acid, where it was indicated that carbonyl groups are not present as such, i.e., that isonitroso ketones cannot be found.

The possibility of nitrogen being present in oxonium structures: $>O.HNO_3$ must also not be overlooked, especially in view of the tendency of the products to form addition compounds with metallic salts. Groups of this nature would be expected to be split off and reduced to ammonia by the alkaline reduction. Since, however, both nitroso and nitro groups may be eliminated by this procedure no quantitative or even qualitative deduction could be drawn regarding oxonium nitrogen.

High-pressure hydrogenation

The nitrohumic acid fraction was subjected to a high-pressure hydrogenation at 2,300 lb. sq. in. and 200° C. in the presence of phenol. Three products were obtained:—

- (1) An amorphous yellow product, soluble in methyl ethyl ketone.
- (2) An amorphous brown product, insoluble in methyl ethyl ketone.
- (3) A light-yellow viscous oil with a green fluorescence. (Yield 5 per cent of the starting material; b.p. ca. 110° C. high vacuum.)

From analysis and the molecular weight determination the molecular formula $C_{14}H_{21}O_8$ was calculated for this oil. In view of the small quantity of oil obtained, no further experiments could be conducted on it. The H/C atomic ratio of the liquid suggests a hydroaromatic structure.

The formation of a liquid in the high-pressure hydrogenation is interesting in that it indicates that high-pressure hydrogenation can break the large humic acid molecule into smaller units in presence of a dissociating solvent such as phenol.

The liquid contained only 1.0 per cent nitrogen which, therefore, can be regarded as an impurity in the product. Therefore, it appears that heterocyclic nitrogen is not present.

Alkaline permanganate oxidation

By oxidizing the nitrohumic acid fraction with different ratios of alkaline permanganate to humic acid, and determining each time the carbon dioxide and steam volatile acids (calculated as acetic acid) formed, curves were obtained as shown in Fig. 5. The curves indicate that both the quantities of carbon dioxide and steam-volatile acids increase with increasing permanganate-humic acid ratios. Light-yellow ether-soluble acids are formed during the oxidation. These acids are darkened in colour on removal of the solvent from methyl ethyl ketone solutions. The results obtained from the analyses of these products were unreliable presumably due to reaction with methyl ethyl ketone. Traces of colourless crystalline needles were isolated from the oxidation product of the oxidation at a permanganate to humic acid ratio of 3.67:1. At this ratio all the humic acid was destroyed since the oxidation product contained no more ether-insoluble material.

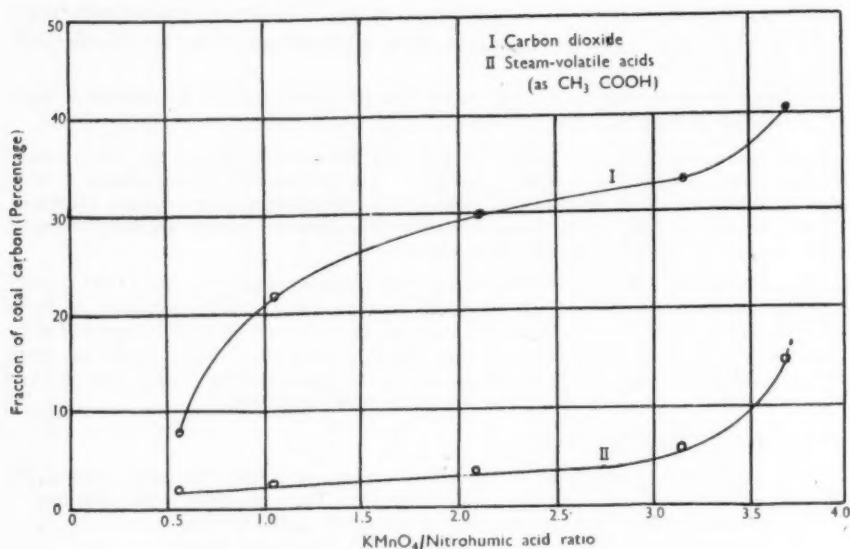


Fig. 5. Alkaline permanganate oxidation of nitrohumic acid fraction I

From this series of experiments the following deductions can be made:—

The nitrohumic acid, which is a product resistant to boiling concentrated nitric acid, can be oxidized by alkaline permanganate to:

- Carbon dioxide.
- Steam-volatile acids.
- Crystalline products.
- Coloured ether-soluble acids.

The formation of (a) and (b) indicates the presence of non-aromatic carbon atoms in the structure, i.e., aliphatic chains and/or hydroaromatic structures.

EXPERIMENTAL

Methylation with methanol and hydrochloric acid gas followed by diazomethane

The nitrohumic acid (0.5 g.) was methylated first with methanol in presence of hydrochloric acid gas and then by treatment with diazomethane in ether at 0°C . The product was purified by reprecipitation and dried at 50°C . in a high vacuum.

6.805 mg. gave 8.984 mg. AgI.

Found: OCH_3 , 17.47 per cent

Hydrolysis of ester groups in the methylation product: The methylation product from the previous experiment (0.1 g.) was heated at 100°C . with dilute alkali (50 ml.; 2 N.) for half an hour when hydrolysis was complete (i.e. the product had dissolved in alkali and no material could be extracted from the alkaline solution by methyl ethyl ketone.) The solution was acidified, extracted with methyl ethyl ketone and the product obtained, purified and dried in the usual manner.

5.157 mg. gave 2.362 mg. AgI.
Found: OCH_3 , 6.04 per cent

Methylation of the silver salt with methyl iodide in a sealed tube followed by methylation with diazomethane

The nitrohumic acid (1 g.) dissolved in acetone (10 ml.) was neutralized with dilute ammonia (2 N, 2.5 ml.) and the excess ammonia boiled off. The neutral solution was filtered and an excess of aqueous silver nitrate (10 per cent; 15 ml.) added. The colourless supernatant liquid was poured off and the precipitate washed three times by decantation with distilled water (50 ml.). The precipitate was filtered on a sintered glass funnel and washed with distilled water until peptization commenced. The precipitate was dried in a vacuum desiccator at room temperature. The dry silver salt (1.0 g.) was methylated with methyl iodide (2.5 g.) by heating in a sealed tube at 100°C . for four hours. The contents were extracted with ether to remove the excess methyl iodide and iodine and then with acetone until the extract was colourless. The acetone extract was filtered, evaporated to a small volume (10 ml.) and the methylation product precipitated by addition of ether (40 ml.). The yellow precipitate was suspended in ether and methylated with diazomethane. The product was dried for three hours in a high vacuum at 50°C .

5.844 mg. gave 9.514 mg. AgI.
Found: OCH_3 , 21.51 per cent

The product was hydrolysed with alkali as described above, purified and dried in the usual manner.

5.204 mg. gave 3.398 mg. AgI.
Found: OCH_3 , 8.63 per cent

Decarboxylation in quinoline in the presence of phenol

Phenol (2 g.) was dissolved in quinoline (10 ml.) by heating. Copper powder (0.1 g.) was added and the mixture heated to 210°C . The nitrohumic acid (0.5 g.) in finely divided form was added in small amounts at a time over a period of 15 minutes, whilst maintaining a temperature of 210° to 215°C . The container was fitted with a reflux condenser and the mixture heated for a further period of one-and-a-half hours. Methyl ethyl ketone (20 ml.) was added and the suspension filtered off. A dark-brown residue was left on the filter. The filtrate was acidified with aqueous hydrochloric acid (V/V; 25 ml.), shaken vigorously and the aqueous layer separated. The methyl ethyl ketone solution of the decarboxylation product (I) was washed with a further quantity of acid and the solvent removed under reduced pressure. The residue was extracted with ether to remove phenol, taken up in acetone and precipitated by the addition of ether. A light chocolate-brown amorphous product was obtained (I, 70 mg.). The methyl ethyl ketone-insoluble residue from the extraction was extracted with pyridine in a Soxhlet apparatus for eight hours. The solvent was removed under reduced pressure and the product precipitated from a pyridine solution by addition of ether. Pyridine was removed and the products dried in the usual manner. The product (0.329g; II) was dark-brown and amorphous.

Product I 3.775 mg. gave 8.740 mg. CO_2 and 1.510 mg. H_2O .
3.493 mg. gave 0.081 ml. N_2 at 750 mm. and 21°C .
Found: C, 63.13; H, 4.47; N, 2.66 per cent.

Product II 3.600 mg. gave 8.917 mg. CO_2 and 1.135 mg. H_2O .
3.597 mg. gave 0.132 ml. N_2 at 750 mm. and 21°C .
Found: C, 67.54; H, 3.52; N, 4.21 per cent.

Both products were methylated with diazomethane in the usual manner.

Methylation product of I

3.658 mg. gave 2.575 mg. AgI.
Found: OCH_3 , 9.30 per cent.

Methylation product of II

5.022 mg. gave 2.247 mg. AgI.
Found: OCH_3 , 5.92 per cent

Reduction by Clemmensen's method: (L. Gattermann, *Laboratory methods of organic chemistry*, London, McMillan and Company, 1935, 24th Ed., p. 383; E. Clemmensen, Ber., 1914, 47, 683.) The nitrohumic acid (0.5 g.) was added to zinc amalgam (7 g.; prepared from zinc and mercuric chloride (Gattermann, loc. cit.)). Concentrated hydrochloric acid (5 ml.) and water (25 ml.) were added and the mixture boiled under reflux, whilst stirring, for seven hours. Concentrated hydrochloric acid (2 ml.) was added after each hour. The reduced product was extracted, metallic salts being removed beforehand by sodium carbonate. The dark-brown amorphous product (0.30 g.) was purified by reprecipitation and dried in the usual manner.

3.795 mg. gave 6.745 mg. CO_2 and 1.350 mg. H_2O ; res. 0.155 mg.
3.455 mg. gave 0.056 ml. N_2 at 750 mm. and 21°C .
Found: C, 50.33; H, 4.15; N, 1.94 (ash-free).

Reaction of the Clemmensen reduction product with nitrous acid

The Clemmensen reduction product (0.5 g.) was dissolved in a minimum of ethanol (10 ml.). Aqueous hydrochloric acid (20 ml.; V/V) was added. The reduced acid was precipitated as a fine suspension. The suspension was cooled in an ice-salt mixture. A solution of sodium nitrite (5 g. in 15 ml. water) cooled to 5°C . was added whilst stirring the solution. The temperature was kept below 5°C . during the addition of the sodium nitrite. The product was extracted with a methyl ethyl ketone-ethanol mixture (500 ml.; 3 parts ketone:1 part other), the solvent removed under reduced pressure and the residue taken up in ethanol and boiled under reflux for 30 minutes. The product was precipitated by the addition of ether to a concentrated solution in ethanol. The brown amorphous product (0.29 g.) was purified by reprecipitation and dried in the usual manner.

3.970 mg. gave 8.150 mg. CO_2 and 1.490 mg. H_2O .
3.602 mg. gave 0.051 ml. N_2 at 750 mm. and 21°C .
Found: C, 55.98; H, 4.19; N, 1.62 per cent.

Determination of carbonyl groups with aluminium-iso-propoxide: Aluminium-iso-propoxide (3 g.: Preparation: A.I. Vogel, *A textbook of practical organic chemistry*, London and New York, Longmans, Green and Company, 1948, p. 815) was dissolved in dry isopropyl alcohol (25 ml.) and distilled on a waterbath. The distillate gave no colouration with Legal-Rimini reagent (sodium-nitroprusside and alkali; Meyer-Jacobson, *Lehrbuch der Organischen Chemie*, 1903, Leipzig, v. Veit, 2nd Ed., I (Teil I), pp. 689 and 734). A control test with acetone was positive. The pure acetone-free nitrohumic acid (0.5 g.) was added to the aluminium-iso-propoxide solution in isopropyl alcohol and the distillation continued. The distillate was also negative to the Legal-Rimini test.

Opening of heterocyclic oxygen rings with the monomethyl ether of ethylene glycol

(W. Fuchs and A. O. Horn, Brenn.-Chem., 1931, 12, 65; W. Fuchs, Ber., 1929, 62, 2125). The nitrohumic acid (1 g.) was dissolved in methyl glycol (10 ml.; b.p. 120° to 125°C .; prepared from methyl iodide, ethylene glycol and sodium (N. Palomaa, Ber., 1902, 35, 3299; M. Palomaa, *ibid.*, 1909, 42, 3873)). Concentrated hydrochloric acid

(0.15 ml.) was added and the mixture boiled under reflux for four hours. The resultant solution was diluted with water and the product extracted with methyl ethyl ketone (100 ml.). The solvent was removed under reduced pressure and the brown amorphous product (0.60 g.) purified by reprecipitation and dried in the usual manner.

4.075 mg. gave 8.000 mg. CO_2 and 1.180 mg. H_2O ; res. 0.055 mg.

3.488 mg. gave 0.077 ml. N_2 at 750 mm. and 21°C .

5.310 mg. gave 2.619 mg. AgI.

Found: C, 45.26; H, 3.28; N, 2.57 (ash-free). OCH_3 , 6.52 per cent.

Nitrogen estimations

A. Determination of total nitrogen by Kjeldahl's method

The accurately weighed nitrohumic acid (0.5-1.0 g.) was digested with concentrated sulphuric acid (20 ml.) until the solution assumed a light straw-yellow colour (40 hours). The ammonia evolved was determined in the usual way.

| | | | |
|---|-----|-------|-------|
| Weight of material (grams) ... | ... | 0.643 | 0.671 |
| Volume N. sulphuric acid used (ml.) ... | ... | 0.88 | 0.94 |
| Total nitrogen (per cent) ... | ... | 1.91 | 1.96 |

B. Determination of nitrogen evolved as ammonia by reduction followed by oxidation Procedure I

(a) *Distillation with zinc dust and alkali*: Zinc dust (5 g.) and distilled water (200 ml.) were added to the nitrohumic acid (0.5-1.0 g.) and the ammonia evolved determined as described in (A) above. More zinc (2 g.) and alkali (200 ml.; 15 per cent) were added and the ammonia evolved again determined in the usual manner.

(b) *Distillation with alkaline permanganate*: To the residue in the distillation flask from determination (a), solid potassium permanganate (10 g.) and distilled water (200 ml.) were added. The solution was distilled into standard acid and the ammonia determined by titration. More permanganate (5 g.) and distilled water (200 ml.) were added and the solution distilled as usual, and the ammonia which evolved again determined by titration.

(c) *Distillation with zinc and alkali*: To the residue in the distillation flask from determination (b), zinc dust (5 g.) and aqueous alkali (200 ml.; 30 per cent) were added. The ammonia which evolved was distilled into standard acid and determined by titration as usual. More zinc (1 g.) and aqueous alkali (200 ml.; 15 per cent) were added and the ammonia determined as usual.

| | Stage | I | II |
|--|-------|-------|-------|
| Weight of material (grams) ... | | 0.653 | 0.632 |
| Volume N. sulphuric acid used (ml.) ... | (a) | 0.24 | 0.24 |
| | (b) | 0.64 | 0.64 |
| | (c) | 0.196 | 0.196 |
| Nitrogen evolved as Ammonia (per cent N) ... | (a) | 0.52 | 0.54 |
| | (b) | 1.37 | 1.41 |
| | (c) | 0.43 | 0.42 |

Procedure II

(a) *Reduction with zinc dust and acid followed by distillation with alkali:* The accurately weighed nitrohumic acid (0.5–1.0 g.) was added to aqueous hydrochloric acid (150 ml.; V/V), zinc dust (2 g.) and ethanol (15 ml.) added and the mixture boiled under reflux for 16 hours. A small amount of zinc dust (0.5 g.) was added every two hours. The suspension was then transferred to a Kjeldahl distillation apparatus and an excess alkali (200 ml.; 40 per cent) added. The ammonia evolved by distillation was absorbed in standard sulphuric acid and estimated by titration.

(b) *Oxidation with alkaline permanganate:* The residue in the distillation flask from (a) above was oxidized with alkaline potassium permanganate and the ammonia evolved by distillation determined in exactly the same manner as was described in procedure I.

(c) *Reduction with zinc dust and alkali:* The residue in the distillation flask from (b) above was treated with zinc dust and alkali and ammonia evolved by distillation determined in exactly the same manner as was described in procedure I.

| | Stage | I | II |
|--|-------|-------|-------|
| Weight of material (grams) | | 0.722 | 0.959 |
| Volume N. sulphuric acid used (ml.) | (a) | 0.29 | 0.40 |
| | (b) | 0.66 | 0.865 |
| | (c) | 0.24 | 0.34 |
| Nitrogen evolved as ammonia (per cent N.) | (a) | 0.55 | 0.57 |
| | (b) | 1.28 | 1.26 |
| | (c) | 0.46 | 0.49 |

Procedure III

(a) *Oxidation with alkaline permanganate:* The accurately weighed nitrohumic acid (0.5–1.0 g.) was oxidized with alkaline permanganate and the ammonia evolved by the process distilled and determined in exactly the same manner as was described in procedure I.

(b) *Reduction with zinc dust and alkali:* The residue in the distillation flask from (a) above was treated with zinc dust and alkali and the ammonia evolved by distillation determined in the usual manner.

| | Stage | I | II |
|--|-------|-------|-------|
| Weight of material (grams) | | 0.436 | 0.762 |
| Volume N. sulphuric acid used (ml.) | (a) | 0.23 | 0.46 |
| | (b) | 0.17 | 0.34 |
| Nitrogen evolved as ammonia (per cent N.) | (a) | 0.73 | 0.84 |
| | (b) | 0.55 | 0.63 |

Alkali treatment

The reprecipitated nitrohumic acid (1.0 g.) was treated with dilute alkali (100 ml.; 2N) by heating first at 100° C. for two-and-a-half hours and then by boiling briskly for another half an hour. The dark-brown solution was acidified, extracted with methyl ethyl ketone and the solvent removed under reduced pressure. The residue (0.8 g.) was taken up in acetone, precipitated with ether and dried as usual.

3.720 mg. gave 6.960 mg. CO₂ and 1.02 mg. H₂O.

3.291 mg. gave 0.108 ml. N₂ at 750 mm. and 21° C.

Found: C, 51.02; H, 3.06; N, 3.76 per cent.

The product was methylated with diazomethane to yield a dark-brown amorphous product.

6.483 mg. gave 9.636 mg. AgI.

Found: OCH₃, 19.66 per cent.

Reaction of the alkali-treated product with nitrous acid

The alkali-treated product (0.2 g.) from the previous experiment was dissolved in a minimum of ethanol (10 ml.) and aqueous hydrochloric acid (25 ml.; V/V) added. The product was precipitated by the acid as a fine suspension. Sodium nitrite solution (10 ml.; 30 per cent) was added, while stirring the solution, over a period of 0.5 hour. The product was extracted with methyl ethyl ketone and the solvent removed under reduced pressure. The residue was taken up in acetone and precipitated by the addition of ether. The amorphous brown product (0.15 g.) was purified and dried in the usual manner.

3.400 mg. gave 5.710 mg. CO₂ and 0.925 mg. H₂O; res. 0.300 mg.

3.718 mg. gave 0.108 ml. N₂ at 750 mm. and 21° C.

Found: C, 50.22; H, 3.34; N, 3.62 per cent (ash-free).

Reduction with titanous-chloride

The alkali-treated product (0.5 g.) from the previous experiment was reduced with titanous chloride and hydrochloric acid and the product extracted as described above. The ethanol-soluble product (0.3 g.) was a dark-brown amorphous substance which was purified by reprecipitation and dried in the usual manner.

4.110 mg. gave 8.465 mg. CO₂ and 1.470 mg. H₂O; res. 0.085 mg.

3.427 mg. gave 0.036 ml. N₂ at 750 mm. and 21° C.

Found: C, 57.35; H, 4.08; N, 1.23 per cent (ash-free).

High-pressure hydrogenation

(a) *Hydrogenation*: The reprecipitated nitrohumic acid (10 g.) was added to a solution of phenol (10 g.) in absolute ethanol (20 ml.) and Raney-nickel catalyst (Preparation: E. Mozingo, Organic Synthesis, Ed. F. H. Allen, New York, John Wiley and Sons, Inc., 1941, p. 15; 5 g.) added. The data for the hydrogenation were as follows:—

| | | | | | |
|---|-----|-----|-----|-----|-------------------------------|
| Initial pressure of bomb | ... | ... | ... | ... | 1,450 lb./sq. in. at 23° C. |
| Time required to raise temperature to 200° C. | ... | ... | ... | ... | 1.5 hours. |
| Pressure at 200° C. | ... | ... | ... | ... | 2,300 lb./sq. in. |
| Time of hydrogenation at 200° C. | ... | ... | ... | ... | 8 hours. |
| Pressure after cooling | ... | ... | ... | ... | 1,350 lb./sq. in. at 22.5° C. |
| Estimated volume of contents of bomb | ... | ... | ... | ... | 30 ml. |
| Pressure drop... | ... | ... | ... | ... | 100 lb./sq. in. at 23° C. |

At 23° C. the pressure drop corresponding to the absorption of one mole of hydrogen is 850 lb./sq. in.

100

∴ Volume of hydrogen removed: $850 \times 22.4 = 2.63$ litres.

(b) *Separation of hydrogenation products*

(i) *Extraction with ethanol*: The hydrogenation product was washed from the bomb with absolute ethanol, the suspension filtered and the light-brown ethanol-insoluble residue extracted with ethanol in a Soxhlet apparatus for 24 hours by which time the extract was colourless.

(ii) *Separation of the ethanol-insoluble portion*: The light-brown ethanol-insoluble amorphous powder was digested with aqueous hydrochloric acid (100 ml.; 1:1) on a boiling waterbath. The process was repeated until all the nickel had been removed. The residue was washed with an ethanol-ether mixture and finally with ether. The dry powder (4 g.) was boiled under reflux with methyl ethyl ketone, filtered, refluxed with more solvent and the process continued until the extract was colourless (about 24 hours). The solution in methyl ethyl ketone was filtered and the solvent removed under reduced pressure. The dry residue was taken up in a minimum of methyl ethyl ketone, filtered, and precipitated by the addition of ether. The light-brown product (2.0 g.) was dried in a high vacuum at 50° C. for three hours.

3.335 mg. gave 7.630 mg. CO₂ and 1.540 mg. H₂O.

3.848 mg. gave 0.080 ml. N₂ at 761 mm. and 20° C.

Found: C, 62.38; H, 5.16; N, 2.42 per cent.

The methyl ethyl ketone-insoluble portion was dissolved in methyl glycol to which two drops of concentrated hydrochloric acid had been added, filtered and the greater part of the solvent removed under reduced pressure. Addition of ether precipitated a dark-brown amorphous substance (2.0 g.). The product was filtered, washed with ether and dried in a high vacuum at 50° C. for three hours.

3.915 mg. gave 8.460 mg. CO₂ and 1.570 mg. H₂O.

3.852 mg. gave 0.098 ml. N₂ at 761 mm. and 20° C.

Found: C, 58.92; H, 4.48; N, 2.96 per cent.

(iii) *Separation of the ethanol-soluble portion*: The solvent from this fraction was removed under reduced pressure. A dark-brown oil (3.2 g.) was left. The phenol was removed by extraction with water in a separating funnel until the odour of phenol could no longer be detected. The oil was taken up in ether, filtered and the solvent removed. A small amount of an ether-insoluble precipitate (0.5 g.) formed during addition of the ether. The ether-soluble oil, dissolved in ether (25 ml.), was poured on a column of alumina (40 g.). The chromatogram was developed with ether and eluted as indicated in Table V.

(iv) *High vacuum distillation of the liquid*: Fraction I was distilled from a small Hickmann flask at 125°–135° C. (bath temperature) at ca. 1×10^{-4} mm. (Mercury vapour diffusion pump backed by a high vacuum oil-pump). The distillate was a light-yellow liquid. The liquid was then redistilled also in a high vacuum. The final distillate (0.5 g.) was a light-yellow viscous oil which showed a green fluorescence.

3.640 mg. gave 8.230 mg. CO₂ and 2.530 mg. H₂O.

3.964 mg. gave 0.034 ml. N₂ at 760 mm. and 20° C.

0.564 mg. + 4.944 mg. camphor gave depr. 16.80°.

Found: C, 61.65; H, 7.77; N, 1.00%; Mol. Wt., 262.

C₁₄H₂₁O₃ requires: C, 62.45; H, 7.80%; Mol. Wt., 269.

TABLE V
Chromatographic separation of the ethanol-soluble fraction of the high-pressure hydrogenation product

| <i>Eluate</i> | <i>Fraction number</i> | <i>Volume of eluate (ml.)</i> | <i>Nature of residu</i> | <i>Weight of product</i> |
|----------------------------------|------------------------|-------------------------------|---------------------------|--------------------------|
| 2N. caustic soda solution | 3 | 100 | Brown amorphous product | Negligible |
| Acetone | 2 | 10 | do. | do. |
| Ether | 1 | 75 | Viscous orange-brown oil* | 2 g. |

* The dilute solution in ether exhibited a green fluorescence.
The elution of each fraction was continued until the eluate was colourless.

Quantitative oxidation with alkaline permanganate

The accurately weighed nitrohumic acid was oxidized with a known quantity of potassium permanganate in the presence of carbonate-free caustic potash solution. Carbon dioxide was determined by acidification, when no more permanganate was present, and absorption on ascarite. Steam-volatile acids were determined by steam-distillation followed by titration with standard alkali. The results are given in Table VI.

TABLE VI
Results of alkaline permanganate oxidation

| Experiment Number | 1 | 2 | 3 | 4 | 5 |
|---|-------|-------|--------|-------|-------|
| Weight of material (grams) | 2.00 | 2.50 | 2.00 | 2.00 | 2.00 |
| Volume KMnO_4 added (ml.) ... | 20 | 50 | 80 | 120 | 200* |
| Normality of KMnO_4 | 1.81 | 1.66 | 1.66 | 1.66 | 1.97 |
| Parts KMnO_4 :1 part nitrohumic acid | 0.57 | 1.05 | 2.10 | 3.15 | 3.67* |
| Weight of CO_2 (grams) | 0.280 | 0.788 | 1.010 | 1.230 | 1.527 |
| Weight of Carbon as CO_2 | 0.076 | 0.215 | 0.302 | 0.336 | 0.416 |
| Fraction of total C as CO_2 (per cent) | 7.47 | 21.14 | 29.70 | 33.03 | 40.90 |
| Volume N. alkali required by steam-volatile acids (ml.) | 0.72 | 0.83 | 1.38 | 2.20 | 4.44 |
| Weight of steam-volatile acids; as acetic acid (grams) | 0.043 | 0.050 | 0.083 | 0.144 | 0.266 |
| Weight of C as CH_3COOH | 0.017 | 0.020 | 0.0332 | 0.576 | 0.106 |
| Fraction of total C as CH_3COOH (per cent) | 1.67 | 1.96 | 3.26 | 5.66 | 10.42 |

* An excess KMnO_4 was left even after boiling for four hours and standing at room temperature overnight. The excess permanganate was determined by titration. The nitrohumic acid (2.00 g.) used 232.4 ml. N- KMnO_4 .

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INVESTIGATION OF THE FRUIT OF THE STRYCHNOS SPECIES

by

S. P. LIGTHELM, H. M. SCHWARTZ and M. M. Von HOLDT

OPSOMMING

Die olie inhoud van die vrugte van die volgende *Strychnos* spesies is bepaal: *Strychnos coccoloides*, *S. dysophylla* en *S. innocua*, asook die chemiese konstantes van die olies. Die olie inhoud van die vrugte pulp varieer van 0.85 persent in die geval van *S. coccoloides* tot 3.8 persent in die geval van *S. innocua*. Die olie inhoud van die pitte was 0.5 persent. Hierdie resultate is teenstrydig met die resultate van Lehmann wat beweer het dat die vrugte van *S. innocua* 40 persent olie bevat en 'n potensiele bron van olie is.

S. dysophylla word ook die „giftige klapper” genoem, maar die vrugte pulp en pitte is skadeloos vir rotte. Die vrugte van die spesies bevat egter 'n bitter bestanddeel, wat nie geïdentifiseer is nie.

SUMMARY

The oil contents of the fruits of *Strychnos coccoloides*, *S. dysophylla* and *S. innocua* have been determined, as well as the chemical characteristics of the oils. The oil content of the fruit pulp ranged from 0.85 per cent in the case of the *S. coccoloides* to 3.8 per cent in the case of *S. innocua*. The oil content of the kernels was 0.5 per cent. These results do not confirm a report by Lehmann that the kernels of *S. innocua* contain 40 per cent of oil and are a potential source of oil.

S. dysophylla is popularly known as the “poisonous klapper” but the fruit pulp and kernels were found to be non-toxic to rats. The fruit of the species, however, contains a bitter principle, the nature of which was not established.

The *Strychnos* species are members of the Loganiaceae or Strychnine family and are found abundantly in the Northern Transvaal, Natal, Mozambique and Madagascar. The fruits of the species are unusual in structure, they are giant berries with a hard woody rind. The size of the fruits varies from about 1 to 4 in. in diameter, the colour is green when immature but changes to yellow on ripening. The pulp of the ripe fruit has a yellow colour, a penetrating, fruity flavour and is pleasant to eat.¹

As far as the authors are aware the only references in the literature to the oil content of the fruit and kernels of the genus *Strychnos* are in popular articles by Lehmann² on possible sources of vegetable oils in South Africa, in which he states that the fruit pulp of “Mkakwa” (*Strychnos innocua*) contains about 40 per cent of oil and that 400 tons of oil could be produced annually from about 100,000 trees.³ Therefore, it was decided to make a study of the oil content of the fruit of various *Strychnos* species and to determine the analytical characteristics of the oil.

EXPERIMENTAL

The species investigated and the sources of the fruits examined were as follows:

Strychnos innocua, collected in Pondoland.

Strychnos coccoloides, collected in the Waterberg District.

Strychnos dysophylla, collected in the Middelburg-Groblersdal districts.

The oil and moisture contents of the fruits and the physical and chemical characteristics of the oils were determined according to the standard methods of the American Oil Chemists Society.⁴ The linoleic and linolenic contents of the oils were determined spectrophotometrically according to the method of Mitchell, Kraybill and Zschiele.⁵

Tests for the toxicity of the fruit pulp and kernels were carried out in the Department of Pharmacology, University of Cape Town.

A bitter principle was extracted from the fruit pulp with acetone. 35 kg. of wet pulp yielded about 24 g. of a bitter solid. This was soluble in acetone, chloroform, alcohol, ethyl acetate, acetic acid and 5 per cent sodium hydroxide solution. It was insoluble in dilute mineral acids. Qualitative tests for nitrogen and sulphur were negative, nor did it give positive tests with the standard alkaloid reagents.

DISCUSSION

The composition of the fruit of the three *Strychnos* species examined are given in Table I together with the analytical characteristics of the oils. It will be noticed that the oil content of the fruit pulp lies between 1-4 per cent on the fresh basis (3-13 per cent on the dry basis). These figures do not confirm Lehmann's report that the fruit pulp of *S. innocua* has a high oil content and the three species are thus of little interest as a source of oil. The oils moreover are dark coloured and have a fairly high free fatty acid content, so that their value is low.

S. dysophylla is known popularly as the "Poisonous Klapper". Samples of the fruit pulp and kernels, however, were found to be non-toxic when fed *ad libitum* to rats. The pulp does contain a bitter principle. This was shown not to be an alkaloid, but its nature was not established.

TABLE I
(a) Composition of the fruits of the *Strychnos* species

| | <i>S. innocua</i> | <i>S. coccoloides</i> | <i>S. dysophylla</i> |
|--|-------------------|-----------------------|----------------------|
| Weight of fruit (g.) | 67-462 | 73-381 | 94-480 |
| Average (g.) | 168 | 167 | 195 |
| Per cent shells in fruit | — | — | 20.3-37.1 |
| Per cent kernel in fruit | — | — | 8.1-17.7 |
| Oil content of pulp (per cent) | 3.8* | 0.85 | 2.1 |
| Oil content of kernel (per cent) | — | — | 0.5 |
| Moisture content of pulp (per cent) | 66.9 | 71.0 | 78.2 |

* Included the kernels.

(b) Characteristics of *Strychnos* oils

| | <i>S. innocua</i> | <i>S. coccoloides</i> | <i>S. dysophylla</i> |
|---|-------------------|-----------------------|----------------------|
| Colour | Reddish | Reddish | Reddish |
| Specific Gravity (25/25°) | — | — | 0.9208 |
| Refractive Index (25°) | — | — | 1.4673 |
| Acid value | — | — | 10.5 |
| Iodine value (Wijs) | 80.5 | 119.9 | 87.3 |
| Saponification value | 192.1 | 168.6 | 188.4 |
| Acetyl value | 5.5 | 9.2 | 9.7 |
| Reichert Meissel value | 0.2 | 1.6 | 1.6 |
| Polenske value | 0.6 | 0.5 | 0.4 |
| Unsaponifiable material (per cent) | 3.3 | 19.9 | 4.5 |
| Linoleic acid in total acids (per cent) | 1.9 | 19.2 | 12.3 |
| Linolenic acid in total acids (per cent) | 7.2 | 3.2 | 2.4 |

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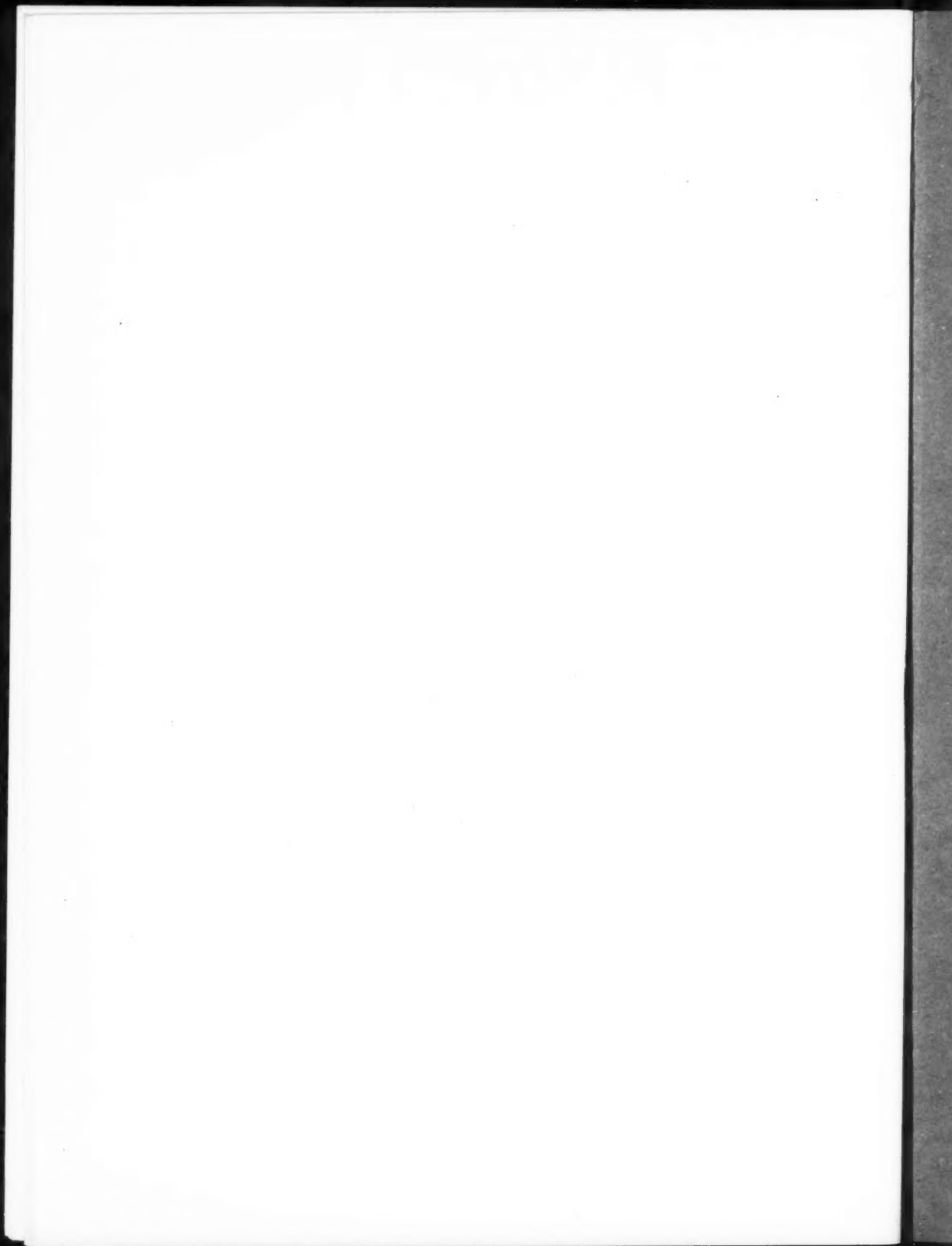
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